Experimentelle Studien an Supraleitern in hohen Magnetfeldern

Experimental Studies on Superconductors in High Magnetic Fields

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Referenten:
Prof. Dr. P. Wyder
Prof. Dr. G. Schatz
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Part I

Einleitung / Introduction
Einleitung


Die in dieser Arbeit vorgestellten experimentellen Untersuchungen an diesen Systemen benutzen die Landau-Quantisierung der Leitungselektronen zur Gewinnung von Informationen über das Leitungselektronensystem und können somit dazu beitragen, das Wesen des elektrischen Transports in diesen Systemen sowie allgemein die Eigenschaften des Elektronensystems besser zu verstehen.


In dieser Arbeit werden Untersuchungen an drei organischen Systemen vorgestellt:
\(\beta-(ET)\_2\text{IBr}_2\), \(\kappa-(ET)\text{Cu(NCS)}_2\) und \(\alpha_T-(ET)\_2\text{I}_3\). In den beiden ersten Fällen wird durch Quantenoszillationsexperimente gezeigt, daß die Niederdimensionalität eine erhebliche Rolle bei der Beschreibung der elektronischen Eigenschaften spielt und es wird der Versuch unternommen, in Vergleichen an zur Zeit vorgeschlagene theoretische Modelle anzuschließen. Das dritte System ist insbesondere wegen seiner für organische Supraleiter verhältnismäßig hohen kritischen Temperatur interessant, die durch einen strukturellen Phasenübergang erreicht wird. Die genaue Natur dieses Überganges ist seit seiner Entdeckung umstritten. In dieser Arbeit werden einige weitere Versuche vorgestellt, sich der elektronischen Struktur dieses Systems experimentell zu nähern, die Ergebnisse und mögliche Ursachen, die eine experimentelle Untersuchung dieses Systems generell erschweren, werden diskutiert.


Im letzten experimentellen Kapitel schließlich werden Vortexnukleationsphänomene in supraleitendem Niob vorgestellt. Die hier vorgestellten Phänomene sind sehr allgemeingültig, nicht nur, daß Vortizes in allen Supraleitern 2. Art auftreten, sondern auch in so verschiedenen Systemen wie Supraflüssigkeiten oder in verschiedenen Modellen des frühen Universums.

Jedes Kapitel dieser Arbeit ist eine eigenständige Untereinheit des Werkes. Querverweise wurden nur gemacht, um Wiederholungen bei der Beschreibung von Methoden zu vermeiden, wenn diese in mehr als einem Kapitel angewendet werden.

Somit legt diese Arbeit zwar einen Schwerpunkt auf einige spezielle Fragestellungen aus dem Bereich der organischen Leiter und Supraleiter, bemüht sich aber, darüberhinausgehend die im Rahmen der Vorbereitung dieser Arbeit zur Verfügung stehenden experimentellen Möglichkeiten auch an daran anschließende und darüber hinausgehende Fragestellungen zu nutzen.
Introduction

Since its discovery by Kammerlingh-Onnes in 1905, superconductivity has been the subject of a large variety of studies, of theoretical as well as of experimental kind. After important basic properties of superconductivity could be described successfully in simple system (elemental metals) by the Ginzburg-Landau theory (macroscopic) and the Bardeen-Cooper-Schrieffer theory (abbreviated BCS, microscopic), the main interest of research was directed towards superconducting systems showing deviations from the BCS-theory. Parallelly to that, the endeavour to obtain superconducting systems with critical temperatures as high as possible to be used in technical applications came up. In order to reach the latter, it is necessary to obtain further experimental data on superconducting systems showing behaviour departing from BCS as well as having a theoretical insight in the phenomena reaching further than BCS. Moreover, the general and basic understanding of those phenomena is subject of controversial discussions.

From BCS theory, the idea of a coupling of two conduction electrons to a pair can be taken over. The BCS theory assumes a phononic coupling of the conduction electrons, but shows also that the precise nature of the coupling is completely irrelevant for the occurrence of superconductivity. The values predicted by the BCS theory for fundamental superconducting parameters are in good accordance with experimental findings for simple systems such as elemental metals.

Organic conductors and superconductors which are the subject of a majority of the experimental studies presented in this work, exhibit behaviour partly deviating from BCS theory. Their synthesis was stimulated by a hypothesis by Little saying that it should be possible to obtain critical temperatures above 1000K in such systems, which would make superconductivity possible at room temperature. After the first systems of this kind could be synthesised, it was soon apparent that neither the critical temperatures predicted by Little could be reached, nor that the special coupling mechanism postulated by Little was realised in these systems. The precise natures of the superconductivity in these systems is, however, still unknown.

The experimental studies on these systems presented in this work make use of the Landau quantisation of the conduction electrons in order to obtain information about the conduction electron system and can thus contribute to a better understanding of the nature of the conductivity of these systems in general.

Such an understanding is not only of fundamental interest, but connects also to other fields of research. At the moment, the highest known critical temperatures are reached by ceramic systems crystallising in a Perowskite structure (e.g. the so-called YBCO-compounds). Because of their sheet structure, these ceramic systems have a structure similar to that of two-dimensional and quasi-two dimensional conductors and superconductors. Thus, it can be assumed that a better understanding of the two-dimensional and quasi two-dimensional organic systems can also promote the understanding of the high temperature superconductors, being of special interest for technical applications.

In this work, experimental studies on three different organic systems are presented: $\beta$(ET)$_2$Br$_2$, $\kappa$(ET)Cu(NCS)$_2$ and $\alpha_T$(ET)$_2$I$_3$. In the first two cases, it is demonstrated by quantum oscillation experiments that the low-dimensionality plays an important role in the description of the electronic properties and an effort is made to compare the results to recently proposed theoretical models. The third system is of special interest because of
its comparably high critical temperature for an organic superconductor, which is induced by a structural phase transition. The exact nature of this transition is unclear since its discovery. In this work, some more efforts to an experimental approach to the electronic structure of this system are presented, the results and possible reasons that generally make the experimental study of this system difficult, are discussed.

The two last experimental chapters go further than the field of organic conductors and superconductors: with the heavy Fermion system CePd$_2$Si$_2$, a system is presented in which magnetic coupling for the generation of superconductivity has been proposed. The results presented here represent the first systematic study with the aim of the experimental determination of the Fermi surface of that system - and thus, of a part of the band structure. Moreover, by direct derivation of the effective electron mass from the quantum oscillation results, its magnetic field dependence is directly demonstrated.

In the last experimental chapter, vortex nucleation phenomena in superconducting niobium are shown. The phenomena presented here are of a very general nature, not only because vortices occur in all superconductors of the second kind, but also in systems as different as superfluid helium and some models of the early universe.

Each chapter is an independent subunit of this work. Cross-references have only been made in order not to repeat the description of several methods and procedures if they are used in more than one chapter.

Thus, this work puts an emphasis on some special problems in the field of organic conductors and superconductors, but also aims at using the experimental possibilities available for the preparation of this work on problems of adjacent or more general kinds.
Part II

Theoretical Considerations
Chapter 1

Quantum Oscillations

This chapter summarises the theoretical description of the magneto oscillatory effects experimentally examined in the framework of this thesis. First, a general account of the quantisation of electron trajectories in a magnetic field is given, then its consequences for magnetisation and electrical resistivity are lined out, i.e. the de Haas-van Alphen effect and the Shubnikov-de Haas effect are presented. The general presentation mainly follows the discussion given in the standard reference [90].

1.1 Landau Quantisation and Onsager Relation

This discussion will follow a semiclassical approach, i.e. the motion of the particle is subject to quantisation, but the forces are not.

1.1.1 Relation of Real Space and Momentum Space

An electron of elementary charge $q_e$ moving in a magnetic field $\vec{B}$ with a velocity $\vec{v}$ experiences a Lorentz force that gives the rate of change of its momentum $\hbar \vec{k}$:

$$\hbar \frac{d\vec{k}}{dt} = -q_e (\vec{v} \times \vec{B}).$$  \hspace{1cm} (1.1)

The integration of equation (1.1) with respect to time directly relates the trajectories in real and momentum space one to another:

$$\hbar \left( \vec{k} - \vec{k}_0 \right) = -q_e (\vec{r} - \vec{r}_0) \times \vec{B}. \hspace{1cm} (1.2)$$

1.1.2 Quantisation of the Motion and Onsager Relation

Closed orbits in real and momentum space correspond to periodic motions to which the Bohr-Sommerfeld quantisation rule can be applied:

$$\oint \vec{p} \cdot d\vec{q} = 2\pi\hbar (n + \gamma) \hspace{1cm} (1.3)$$
CHAPTER 1. QUANTUM OSCILLATIONS

Figure 1.1: Illustration of Landau cylinders in momentum space. (a) Free electrons: the surfaces of constant energy are spherical. (b) Ellipsoidal surfaces of constant energy. From [90].

with $\vec{p}$ and $\vec{q}$ the canonically conjugate momentum and position respectively and $n$ an integer, $\gamma$ a phase factor. Using equation (1.2) and Stokes’ theorem, this can be written in terms of the magnetic flux $\Phi$:

$$\Phi \equiv BA = \frac{2\pi\hbar}{q_e} (n + \gamma)$$  \hspace{1cm} (1.4)

with $A$ the surface of the orbit in real space perpendicular to the magnetic field. Using equation (1.2), this can be re-expressed as the Onsager relation:

$$a_n = \frac{2\pi q_e B}{\hbar} (n + \gamma)$$  \hspace{1cm} (1.5)

giving the area $a_n$ of an orbit in $\vec{k}$-space corresponding to the orbit indexed by $n$.

1.1.3 Degeneracy and the Concept of Landau Cylinders

As seen before, the motion is confined to orbits enclosing surfaces quantised in units of $2\pi q_e B/\hbar$ in the plane perpendicular to the magnetic field. The motion parallel to the magnetic field is not quantised since there is no symmetry breaking by the field in that direction.

This gives rise to a degeneracy of the states corresponding to the orbits enumerated by $n$ as a result of the non-quantised degree of freedom in the direction parallel to the magnetic field which allows for several electrons having the same quantum number $n$ without in the same single particle state. The set of states described by equation (1.5) for a specific value of $n$ therefore corresponds to a cylinder in $\vec{k}$-space as illustrated in figure 1.1. Such a cylinder in $\vec{k}$-space due to a quantisation of orbits as result of a magnetic field is usually referred to as a Landau cylinder, the quantisation of a motion on Landau cylinders when a magnetic field is present, is called Landau quantisation, the energy of the electron system is quantised in Landau levels, each of which corresponds to one Landau cylinder in $\vec{k}$-space.
1.1.4 Onsager Relation and Periodicity

The Onsager Relation (1.5) shows that for increasing magnetic field $B$ the surface of all Landau cylinders in $\vec{k}$-space increases. However, the Fermi surface of the electrons remains constant to a first approximation. As the the thermodynamic properties as well as other important parameters – for example the electric resistivity – of a metallic system are largely controlled by the electrons at the Fermi surface only, it is of interest to know with what regularity the Landau cylinders will cross the Fermi surface since this will change the properties of the whole system with the same periodicity.

The degeneracy of each Landau level is such that each Landau tube accommodates as many electron states as there would be in the annual cross sectional area $\Delta a$ between the Landau tube in question and the neighbouring one in $\vec{k}$-space at zero magnetic field:

$$\Delta a = \frac{2\pi q_e B}{\hbar}$$

(1.6)

according to the Onsager relation (1.5).

As shown by equations (1.5) and (1.6), both, $a_n$ and $\Delta a$ increase with increasing $B$, thus, a Landau level can accommodate more electron states the more intense the magnetic field is.

When the magnetic field is increased, the Landau cylinders are increased in their diameter and will cross the Fermi surface. At some point, they will have crossed the outermost parts of the Fermi surface, this means they are now bigger than the extreme diameter of the Fermi surface $A_{extr}$. Being thus totally out of the Fermi surface, they cannot be occupied by electrons anymore and all electrons that were accommodated in states associated with these particular Landau cylinders must be accommodated in states lying within the Fermi surface. Ultimately, only the last Landau tube will remain within the Fermi surface and no more states within the Fermi surface will be available to accommodate the electrons when that Landau tube crosses the Fermi surface. This is the limit of validity of the theory sketched here. When the field is increased even more, other phenomena have to be taken into account as they are for example described by theories of composite fermions. This limit is usually named the quantum limit.

For the case of sufficiently high $n$, that means unaffected by effects rising from approaching the quantum limit, the difference $\Delta B$ between the fields of two Landau tubes indexed $n$ and $n - 1$ crossing the extremal Fermi surface section area $A_{extr}$ is given according to equation (1.5) as:

$$\Delta \left( \frac{1}{B} \right) = \frac{1}{B} - \frac{1}{B_{n-1}} = \frac{2\pi q_e}{\hbar A_{extr}}$$

(1.7)

The Landau cylinders’ crossing of the Fermi surface is thus periodic in $1/B$ and we can expect the density of states at the Fermi level to oscillate with that periodicity and hence all other parameters depending on that density of states.

A Fourier analysis yields the oscillation frequency $F_{osc}$ on a $1/B$-scale:

$$F = \frac{\hbar}{2\pi q_e A_{extr}}.$$  

(1.8)
CHAPTER 1. QUANTUM OSCILLATIONS

1.1.5 Usefulness and Limits of Quantum Oscillations as Experimental Probes of the Fermi Surface

Since equations (1.7) and (1.8) are valid for any direction of the magnetic field, the observation of quantum oscillations is a useful tool to investigate the shape of Fermi surfaces experimentally. Indeed this has been and still is a widely used tool for that purpose. It should however be kept in mind that this method yields information about the extreme diameters of the Fermi surface only, that means about the parts of the Fermi surface where its first derivative becomes zero and this averaged over the whole cross sectional area. In practise, it is virtually always necessary to fit the data obtained experimentally to a theoretical model in order to obtain a useful result.

Within the framework of this thesis, some experiments were done with the objective to explore an unknown Fermi surface, but an important part of this work is rather consecrated to the attempt to learn something about the deviations from the ideal behaviour as it is described by the theory and thus something about the more subtle, underlying interactions of the electronic system with itself or other parts of the entire system.

1.2 The de Haas-van Alphen Effect

Having thus outlined a rough sketch of the physical reasons for the occurrence of magneto quantum oscillations, this section will be consecrated to a closer look at one of the various effects that originate from that phenomenon. The de Haas-van Alphen effect is the name given to the magnetic field induced oscillations of the magnetisation. These sections outline the standard theoretical description given by Lifshitz and Kosevich in [64] and discusses the impact of various parameters and experimental conditions on the results as predicted by this theory.

1.2.1 Thermodynamic Description

The magnetisation $\vec{M}$ of a system is given by the derivative of the appropriate thermodynamic potential with respect to the magnetic field $\vec{B}$. In the description of a system by the Grand Canonical Potential $\Omega$, this gives:

$$\vec{M} = -\left. \frac{\partial \Omega}{\partial \vec{B}} \right|_\mu$$

(1.9)

where the chemical potential $\mu$ is to be kept constant.

The grand canonical potential for a system of discrete energy levels $E_n$ is given by:

$$\Omega = -k_B T \sum_n \ln \left[ 1 + \exp \left( \frac{\mu - E_n}{k_B T} \right) \right].$$

(1.10)

Here, $k_B$ is the Boltzmann constant and $T$ the temperature of the system, the other symbols used as before. Computing the sum explicitly and subsequently carrying out the derivative (1.9) yields the total magnetisation. The oscillatory part of it is known as the Lifshitz-Kosevich formula:
1.2. The De Haas-Van Alphen Effect

\[ M_{\text{osc}}^\parallel = -\sqrt{\frac{q_e^2}{2\pi^2\hbar}} \frac{F_{\text{osc}}\sqrt{B}}{m^* \sqrt{|A''_{\text{extr}}|}} \cdot \sum_{p=1}^{\infty} \frac{1}{p^{3/2}} R_T(p) R_D(p) R_s(p) \sin \left[ 2\pi p \left( \frac{F_{\text{osc}}}{B} - \gamma \right) \pm \frac{\pi}{4} \right] \]  

(1.11)

for the magnetisation parallel to the magnetic field and

\[ M_{\text{osc}}^\perp = -\frac{1}{F} \frac{dF}{d\theta} M_{\text{osc}}^\parallel \]  

(1.12)

for the magnetisation perpendicular to the magnetic field.

To carry out the summation of the thermodynamic potential (1.10), in a first step only a two-dimensional slab of \( \vec{k} \)-space perpendicular to the magnetic field is considered. The summation is then done considering the degeneracy of each Landau level, usually with the help of the Poisson summation formula [89] or the Euler-MacLaurin formula [61]. In a next step, the states along the field axis are considered by a subsequent integration that effectively only considers extremal Fermi surface cross sectional areas because the contributions of other Fermi surface parts interfere destructively and thus cancel each other. The equations (1.11) and (1.12) are the result of this calculation.

The following symbols have been used in addition to those already defined: \( m^* \) is the effective cyclotron mass of an electron in the corresponding orbit. To a first approximation, it equals the effective mass given by the bandstructure model

\[ m_{BS}^* = \frac{\hbar^2}{2\pi} \frac{\partial A}{\partial E}. \]  

(1.13)

Corrections to this may occur from electron-electron and phonon-electron interactions. \( A''_{\text{extr}} \) is the second derivative of the extremal Fermi surface cross-sectional area with respect to the \( \vec{k} \)-component parallel to the magnetic field:

\[ A''_{\text{extr}} = \left( \frac{\partial^2 A_{\text{extr}}}{\partial k_\parallel^2} \right). \]  

(1.14)

The indexed factors \( R \) are amplitude factors that will be explained in the following subsections.

1.2.2 Temperature Factor \( R_T \)

This factor accounts for the effect of a finite temperature \( T > 0 \). Such a temperature leads to a broadening of the energy distribution of the electrons described by the Fermi-Dirac distribution:

\[ f(E) = \frac{1}{1 + \exp \left( \frac{E - \mu}{k_B T} \right)}. \]  

(1.15)
and thus leading to contributions not originating from electrons at the exact Fermi energy, but also from electrons at energies near the Fermi energy. This gives rise to the temperature amplitude factor

$$R_T(p) = \frac{\alpha p m^* T}{\sinh (\alpha p m^* T / B)}$$

where the abbreviation

$$\alpha = \frac{2\pi^2 k_B m_e}{\hbar q_e} \approx 14.69 T/K$$

is used.

### 1.2.3 Dingle Factor $R_D$

The Dingle factor $R_D$ describes the effect of electron scattering. The underlying formalism is a relaxation time ansatz assuming a Lorentzian broadening of the otherwise sharp Landau energy levels. For a relaxation time $\tau$, this ansatz gives rise to another amplitude factor, the Dingle Factor $R_D$:

$$R_D = \exp \left( -\alpha p \frac{m^* T_D(\tau)}{m_e B} \right)$$

where the relaxation time $\tau$ determines the parameter $T_D$:

$$T_D = \frac{\hbar}{2\pi k_B \tau}.$$  

The parameter $T_D$ has the dimension of a temperature and is usually referred to as the Dingle temperature. It is a measure of the scattering relaxation time and can thus be used to specify the crystal quality of a particular sample.

### 1.2.4 Spin Factor $R_s$

This factor describes the effect of the fact that an electron with a spin 1/2 can have two different orientations with respect to a field $\vec{H} = \vec{B} + \mu_0 \vec{M}$ with energies differing by

$$\Delta E = \frac{1}{2} g \beta_0 H$$

where $\beta_0 = q_e h / m_e c = 2$ Bohr magnetons and $g$ is the so-called spin-splitting factor of the particular system. The main consequence of (1.20) is a splitting of each Landau level into two levels separated by $\Delta E$ and thus to two different sets of oscillations interfering with each other. Equation (1.20) shows that the importance of this effect increases with increasing field $H$.

The formal treatment of this phenomenon gives rise to the spin reduction factor

$$R_s(p) = \left| \cos \left( \frac{\pi}{2} g \beta_0 \frac{m^*}{m_e} \right) \right|.$$
1.3. THE SHUBNIKOV-DE HAAS EFFECT

It is worth noting that this effect can even make the oscillation of a specific harmonic vanish completely if the cosine in equation (1.21) becomes zero. This is the case if

\[ pg \frac{m^*}{m_e} = 2n + 1. \]  

(1.22)

This phenomenon is usually known as spin zero. Due to their dependence on \( p \), the spin zeros occur at different angles for each harmonic component.

1.2.5 Special Conditions in Two-Dimensional Systems

In a two-dimensional system, the Fermi surface curvature \( A'' \) in equation (1.11) tends to zero, therefore the magnetisation as given by the Lifshitz-Kosevich formula (1.11) would diverge. Consequently, a different approach to this problem is necessary.

Contrary to the three-dimensional case, in the two-dimensional case the Landau cylinders pass the Fermi surface very abruptly. This is due to the cylindrical shape of the latter which makes it impossible for a Landau cylinder to pass ”smoothly” as it is possible in the three dimensional case where the Landau cylinder intersects with the Fermi surface within a certain field range, whereas in the two-dimensional case the crossing corresponds to one field value only.

The consequence of the latter circumstance is a field-dependence of the chemical potential \( \mu \) [90] that must be considered in a theoretical description. The development of such a theory is a still uncompleted task. Recent work is represented by [101] [100] [48] [46] [47] [39] [34] [17].

1.3 The Shubnikov-de Haas Effect

The appearance of oscillatory effects in the conductance or resistivity as a function of magnetic field due to Landau quantisation is referred to as the Shubnikov-de Haas effect. Historically, it was discovered before the de Haas-van Alphen effect [92] [22]. Although the physical origin of the Shubnikov-de Haas effect is the same as for the de Haas-van Alphen effect, i.e. the Landau quantisation, they are of different nature. Whereas the de Haas-van Alphen effect is a purely thermodynamic property, the Shubnikov-de Haas effect is a transport property. As such, its description includes transport processes that do not contribute to purely thermodynamic phenomena as the de Haas-van Alphen effect.

1.3.1 Adams-Holstein Theory

The standard theory to describe the Shubnikov-de Haas effect was developed by Adams and Holstein and published in 1959 [4]. The calculation is rather extended and only the most important results will be quoted here.

Before looking at the quantitative result, it is helpful to regard a qualitative argument already used by Adams and Holstein themselves and discussed in more detail by Pippard [74].

This argument runs mainly as follows: the probability for an electron to be scattered is proportional to the matrix element describing the scattering potential and the number
of states into which it can be scattered. To a good approximation, the matrix element remains constant and unaffected by the Landau quantization. On the other hand, the number of accessible states varies with the field as it is given as the convolution of the density of states as a function of energy and the Fermi-Dirac distribution. Thus, the number of states is greatly increased when a Landau cylinder crosses the Fermi surface and scattering is very probable then. If there is no Landau cylinder at the Fermi surface, the number of available states for scattering is low. As scattering is the main origin of the electrical resistivity, the resistivity and its inverse, the electrical conductivity, will be affected by a change of the scattering probability. The scattering probability oscillates with the Landau cylinders crossing the Fermi surface with a periodicity in $1/B$ and so the conductivity or respectively the resistivity can be expected to have an oscillatory contribution of that periodicity as well.

The more quantitative argument by Adams and Holstein includes a detailed mathematical description of the scattering process, so that the detailed properties of the oscillatory effect can be expected depend on the specific scattering process. However, Adams and Holstein performed the detailed calculation for two different scattering processes, namely phonon and ionized impurity scattering, deliberately choosing two scattering processes very different in nature. It turns out, however, that these very different scattering processes generate oscillatory effects being comparable in size. Thus, they conclude, that the nature of the scattering process involved does not play an important role.

In their final result, Adams and Holstein describe the total conductivity as a function of the magnetic field as the sum of the classical background conductivity $\sigma_0(B)$ and two quantum correction terms $\Delta \sigma_1(B)$ and $\Delta \sigma_2(B)$ containing the oscillatory contributions:

$$\sigma_{xx}(B) = \sigma_0(B) \left[ 1 + \Delta \sigma_1(B) + \Delta \sigma_2(B) \right].$$

(1.23)

Physically, the term $\Delta \sigma_1$ describes scattering from the highest occupied Landau level, i.e. at the Fermi surface, to levels above the Fermi surface, so-called inter-level scattering, whereas the term $\Delta \sigma_2$ describes scattering within the highest occupied Landau level, so-called intra-level scattering. Usually, the intra-level scattering term can be neglected if the system is far from the quantum limit, i.e. $F/B >> 1$.

Expressing equation (1.23) in terms of steady and oscillatory parts of the electronic density of states, $D_0$ and $D_{osc}$ respectively, equation (1.23) becomes:

$$\sigma_{xx}(B) = \sigma_0(B) \left\{ 1 + R_T \left[ \frac{5}{2} \frac{D_{osc}(B)}{D_0(B)} + \left( \frac{3}{2} \frac{D_{osc}(B)}{D_0(B)} \right)^2 \right] \right\}.$$  

(1.24)

The density of states at the Fermi level $D$ is now obtained from the thermodynamic potential $\Omega$.

The thermodynamic potential $\Omega$ for fermions is given by

$$\Omega = -k_B T \int D(E) \ln \left[ 1 + \exp \left( \frac{\mu - E}{k_B T} \right) \right] dE.$$  

(1.25)

For zero temperature, the density of states at the Fermi edge is thus given by

$$D = -\frac{\partial^2 \Omega}{\partial E^2}.$$  

(1.26)
1.3. THE SHUBNIKOV-DE HAAS EFFECT

With the first derivative with respect to the magnetic field of the thermodynamic potential being known as the magnetisation from equation (1.9), the oscillatory part of the density of states can be written as

\[ D_{osc} = \frac{1}{RT} \frac{m^*}{q_e \hbar} \left( \frac{B}{F_{osc}} \right)^2 \frac{\partial M_{osc}}{\partial B}. \]  \hspace{1cm} (1.27)

The oscillatory part of the resistivity can thus be written in a form that is analogous to the Lifshitz-Kosevich formula (1.11):

\[ \frac{\Delta \sigma_{osc}}{\sigma_0} = \frac{5}{2} \sqrt{\frac{\pi q_e \hbar}{E_f}} \sqrt{\frac{B}{m^* |A''_{extr}|}} \cdot \sum_{p=1}^{\infty} \frac{1}{p^{1/2}} R_T(p) R_D(p) R_s(p) \cos \left[ 2p \left( \frac{F_{osc}}{B} - \gamma \right) \pm \frac{\pi}{4} \right]. \]  \hspace{1cm} (1.28)

Comparing to the Lifshitz-Kosevich formula (1.11), the main differences turn out to be:

- the constant amplitude factors
- the spectrum of harmonics
- a phase shift of 90 degrees or \( \pi/4 \) between the de Haas-van Alphen and the Shubnikov-de Haas oscillations.
Chapter 2

Theories on Superconductivity

This chapter reviews the two theories that are mainly used for the description of superconducting phenomena: the Ginzburg-Landau theory and the Bardeen-Cooper-Schrieffer theory. Whereas the former is a macroscopic theory, i.e. it describes phenomena concerning the superconducting system as a whole without caring about the origin of the phase transition, the latter provides a description of the microscopic mechanisms that are at the origin of the superconducting phase transition. It should also be mentioned that the Ginzburg-Landau theory is not restricted to superconductivity but can also be applied to a variety of other phase transitions.

2.1 Ginzburg-Landau Theory

2.1.1 Introduction

The Ginzburg-Landau theory is a quite general theory describing second order phase transitions. It is a macroscopic theory based on some rather general assumptions about the phase transition to be described. Its application to superconductivity has proven to be particularly fruitful, but it has also been applied successfully to other phase transitions. However, not every second-order phase transition can be described by the Ginzburg-Landau theory, some additional prerequisites have to be fulfilled as well.

The theory was first published in 1950 by Ginzburg and Landau [29]. Later, when the microscopic BCS theory of superconductivity was developed [11], it was shown by Gorkov [30] that for some temperature and magnetic field ranges the macroscopic Ginzburg-Landau equations follow rigorously from the microscopic assumptions of the BCS theory. The brief review of the Ginzburg-Landau theory that is given here follows mainly the presentation of that subject in [95].

2.1.2 The Order Parameter

The Ginzburg-Landau theory assumes that the phase transition can be described by means of an order parameter \( \psi \) in the sense that one of the phases is identified with "order" and the other with "disorder". The order parameter is now a measure of the degree of order in the system, i.e. provides information about which of the two states in question the system is in. In the case of superconductivity, the normal conducting state could for example
be associated with the disordered phase \((\psi = 0)\) and the superconducting state with the ordered phase \((\psi \neq 0)\).

The aim of the theory is now to obtain equations to describe the behaviour of the order parameter \(\psi\). External fields are represented by a vector potential \(\vec{A}\).

### 2.1.3 Basic Assumptions

The Ginzburg-Landau theory treats the occurrence of a phase transitions by minimizing the free energy \(F\). The first basic assumption is that the free energy can be expanded in a power series in \(\psi\):

\[
F \approx F_0 + \lambda \psi + \alpha \psi^2 + \gamma \psi^3 + \frac{1}{2} \beta \psi^4. \tag{2.1}
\]

The second basic assumption is that the coefficients in equation (2.1) can be expanded in a power series in \((T - T_c)\), where \(T_c\) is the critical temperature of the phase transition. The theory is thus valid for temperatures \(T\) that are close to the critical temperature \(T_c\).

In an equilibrium state, \(F\) has a minimum and thus \(\partial F/\partial \psi = 0\). This requires the coefficient \(\lambda\) in equation (2.1) to be zero. As a further approximation, it is also assumed that \(\gamma = 0\).

### 2.1.4 Kinetic Energy Term

Equation (2.1) is now an expression for the total free energy of the system. Regarding \(\psi\) as a function of position, \(F\) is replaced by a free energy density \(f\) the integral of which over the whole volume of the system gives \(F\).

Regarding \(\psi\) as a function of space makes expecting a kinetic energy term proportional to \(|\nabla \psi|^2\). Equation (2.1) thus becomes

\[
f(\vec{r}) = f_0 + \alpha |\psi(\vec{r})|^2 + \frac{1}{2} \beta |\psi(\vec{r})|^4 + \frac{\hbar}{2m_e} |\nabla \psi(\vec{r})|^2. \tag{2.2}
\]

The prefactor of the kinetic energy term follows convention and does not imply any physical meaning [21], \(m_e\) denotes the electron rest mass.

### 2.1.5 Magnetic Field

To consider the effect of an external magnetic field, the nabla operator in equation (2.2) is replaced by \(\nabla - \frac{2q_e}{\hbar} \vec{A}\) and the magnetic field energy is included. Equation (2.2) now becomes

\[
f(\vec{r}) = f_0 + \alpha |\psi(\vec{r})|^2 + \frac{1}{2} \beta |\psi(\vec{r})|^4 + \frac{1}{2m_e} |(-i\hbar \nabla - 2q_e \vec{A}) \psi|^2 + \frac{\hbar^2}{2m_e} \frac{\vec{B}^2}{2\mu_0} - \frac{\mu_0 \vec{H}_0^2}{2}. \tag{2.3}
\]
2.1. GINZBURG-LANDAU THEORY

2.1.6 The Ginzburg-Landau Equations

Equation (2.3) now provides an expression for the Helmholtz free energy density \( f \). In order to obtain the equilibrium state for given temperature \( T \) and field \( H \), the Gibbs free energy

\[
G = F - \vec{H} \cdot \vec{B}
\]

must be minimized. \( G \) is represented by a volume integral over the Gibbs free energy density

\[
g = f - \vec{H} \cdot \vec{B}
\]

with \( f \) being given by equation 2.3. Minimising \( G \) is now done by the usual Euler-Langrange variation formalism. Furthermore, the gauge \( \text{div} \vec{A} = 0 \) is used.

The First Ginzburg-Landau Equation

Variation of \( G \) with respect to \( \psi \) yields the first Ginzburg-Landau equation:

\[
\frac{1}{2m_e} \left( -i\hbar \nabla - 2q_e \vec{A} \right)^2 \psi + \alpha \psi + \beta |\psi|^2 \psi = 0.
\]

(2.6)

The Second Ginzburg-Landau Equation

The second Ginzburg-Landau equation is obtained by carrying out the variation of \( G \) with respect to \( \vec{A} \):

\[
\vec{J} = -\frac{i q_e \hbar}{m_e} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{4 q_e^2}{m_e} \psi^* \psi \vec{A}.
\]

(2.7)

Here, the asterisk '*' denotes the complex conjugate and the current \( \vec{J} \) replaces a term \((1/\mu_0)\text{curl}\vec{B}\) according to Maxwell’s equations.

Both Ginzburg-Landau equations (2.6) and (2.7) now allow to determine \( \psi \) as a function of position for a given external field configuration and temperature.

2.1.7 Temperature Dependence

The temperature dependence of equations (2.6) and (2.7) is included in the coefficients \( \alpha \) and \( \beta \) as follows. If one assumes that \( \lambda \) and \( \gamma \) in equation (2.1) are zero, the equilibrium condition \( \partial F/\partial \psi = 0 \) yields

\[
\alpha \psi_0 + \beta \psi_0^3 = 0.
\]

(2.8)

Requiring that \( \psi_0 \) shall be zero for \( T > T_c \) and nonzero for \( T < T_c \) and that \( F \) shall not indefinitely decrease, one obtains

\[
\alpha(T) = A(T - T_c)
\]

(2.9)

\[
\beta(T) = \beta_0 = \text{const.}
\]

(2.10)

which are the simplest temperature dependencies fulfilling these requirements.
2.1.8 The Abrikosov Vortex Lattice

One of the most prominent consequences of the Ginzburg-Landau theory when applied to superconductors is the occurrence of the Abrikosov vortex lattice when a type-II-superconductor, that is one whose surface energy at a super-/normalconducting boundary is negative, is exposed to an external magnetic field. For fields \( H \) in between two critical fields \( H_{c1} < H < H_{c2} \), the field penetrates the superconductor locally in the form of magnetic flux vortices, the so-called Abrikosov vortices that can occur arranged in a regular, periodic lattice, the Abrikosov vortex lattice. The result was first obtained by Abrikosov in 1957 [2].

Abrikosov’s original calculation is valid for the limit \( H \to H_{c2} \). In this limit, the first Ginzburg-Landau equation (2.6) can be linearised as follows: the order parameter \(|\psi|^2\) is small everywhere near \( H_{c2} \), so the term \( \beta |\psi|^2\psi \) in equation (2.6) can be neglected. Furthermore, the field variation as a function of spatial co-ordinates is small, so the vector potential for a uniform applied field \( \vec{H}_0 = (0, \mu_0 H_0 x, 0) \) can be used, here in the gauge \( \vec{A} = (0, \mu_0 H_0 x, 0) \). Applying these simplifications, equation (2.6) can be rewritten as

\[
-\frac{\hbar^2}{2m} \partial^2 \psi + \frac{1}{2m} \left( -i\hbar \frac{\partial}{\partial y} - 2q e \mu_0 H_0 x \right)^2 \psi - \frac{\hbar^2}{2m} \partial^2 \psi = |\alpha| \psi. \tag{2.11}
\]

For the solution of equation (2.6) and (2.7) an ansatz of the form \( \psi = \psi_L + \psi_1 \) is made where \( \psi_L \) is a solution of the linearized equation (2.11). Additionally, \( \psi_L \) and \( \psi_1 \) are required to be orthogonal.

In order to solve for \( \psi_L \), a general linear combination of solutions to equation (2.11) is chosen

\[
\psi_L(x, y) = \sum_n C_n \exp(inky) \exp \left[ -\frac{(x - x_0)^2}{2\xi^2(T)} \right] \tag{2.12}
\]

where \( x_n = n \hbar k / 2q e \mu_0 H_{c2} = nk \xi^2(T) \) and \( \xi \) is the coherence length. Furthermore, a periodicity condition is imposed:

\[
C_{n+N} = C_n. \tag{2.13}
\]

The choice of \( N \) determines the exact geometry of the solution. So far, only the cases \( N = 1 \) [2] and \( N = 2 \) [56] have been considered.

Without going through the details of the further calculation that can for example be found in [2] or [95], just the main results shall be cited here. The general result without considering the exact form of the lattice gives the following condition for \( \psi_L \):

\[
(2\kappa^2 - 1) \frac{q e \hbar}{m} \left\langle |\psi_L|^4 \right\rangle = (H_{c2} - H_0) \left\langle |\psi_L|^2 \right\rangle \tag{2.14}
\]

using the notation

\[
\int |\psi_L|^n d^3r = \langle |\psi_L|^n \rangle. \tag{2.15}
\]

The parameter \( \kappa \) is defined as the ratio of penetration depth \( \lambda \) and coherence length \( \xi \) as \( \kappa = \lambda / \xi \). Note that \( \kappa > 1 / \sqrt{2} \) is required to solve equation (2.14), which is the condition for a superconductor being of type II.
2.1. GINZBURG-LANDAU THEORY

The magnetisation is then given by

\[ M = -\frac{\mu_0 (H_{c2} - H_0)}{(2\kappa^2 - 1) \beta_A} \]  

(2.16)

where

\[ \beta_A = \frac{\langle |\psi_L|^4 \rangle}{\left( \langle |\psi_L|^2 \rangle \right)^2} \]  

(2.17)

and the notation of (2.15) is used again. Equation (2.16) now shows that the Gibbs free energy (2.4) decreases as \( \beta_A \) decreases. An appropriate choice on the exact geometry of the lattice must now be made by adjusting the periodicity condition (2.13) in order to find the geometry that corresponds to a minimum of the Gibbs free energy. Abrikosov chose \( N = 1 \) yielding \( \beta_A = 1.18 \) and a square lattice. Kleiner et al. showed later that the choice \( N = 2 \) together with \( C_1 = \pm C_0 \) yields a square lattice with \( \beta_A = 1.16 \) [56]. This latter geometry is confirmed by experimental findings [25]. Figure 2.1 illustrates the two geometries.

2.1.9 Fluctuations and Vortex Dynamics, Pinning

The Abrikosov vortex lattice represents the lowest-energy equilibrium ground state of the vortex many-quasiparticle system. Other states, however do exist. Other geometries of the lattice or disordered vortex glass states may occur as temperature and other thermodynamical parameters vary and sufficient energies for transitions to such states is provided. The system can then cross over to such different states and fluctuations between them can occur as a result of thermal excitation.

In a disequilibrium situation vortices can move through the superconductor. In this process, energy is dissipated that manifests itself as an electric potential difference \( V_{\text{diff}} \) perpendicular to the vortex velocity vector \( \vec{v}_{\text{vortex}} \). The physical reason for the occurrence of the dissipation is the fact that the phase of the vortex quantum mechanical wave function

![Figure 2.1: Level surfaces of \( |\psi_L|^2 \) in the square geometry (N=1, left) [2] and in the triangular geometry (N=2, right) [56].](image)
changes when going around the vortex, but must be coherent with that of the whole vortex system. A moving vortex thus modifies the wave function of the whole system which results in an electrochemical potential difference of the vortex system. This concept of phase slip has been introduced by Anderson [5].

The potential difference is then given by

$$\frac{2q_e}{\hbar} V_{diff} = 2\pi n$$

(2.18)

where $n$ denotes the number of vortices per second passing the line between the two points where the voltage difference is observed.

The direction of the vortex flow is along the electrochemical potential gradient

$$\frac{d\bar{p}}{dt} = -\nabla \mu = \bar{F}$$

(2.19)

but additionally, as each vortex carries one magnetic flux quantum $\Phi_0$, a Lorentz force

$$\bar{F}_{Lorentz} = \bar{J} \times \Phi_0$$

(2.20)

acts on each vortex. This can lead to different directions of the vortex velocity $v_{vortex}$ and the transported electrical current $\bar{J}$. The presence of an external magnetic field adds to this Lorentz force.

A vortex can however be hindered from moving by impurities or lattice defects in the superconductor. The vortex then remains immobilized in the position were the defect occurs. This process is known as pinning.

2.1.10 Time-Dependent Ginzburg-Landau Theory

The Ginzburg-Landau theory as it has been presented so far is a theory describing the equilibrium state of a system. In order to describe the relaxation of a system from disequilibrium into equilibrium, the theory has to be extended to include time-dependent phenomena. The argument presented here follows Gorkov and Kopnin [31] who take up an idea by Schmid [82].

The extension is done on phenomenological grounds. The order parameter $\psi$ is assumed to relax slowly and its rate of change is assumed to be linked to the free energy $F$ of the system as follows:

$$\eta \frac{\partial \psi}{\partial t} = -\frac{\partial F}{\partial \psi}$$

(2.21)

following the standard ansatz for slowly relaxing parameters where $\eta$ is a proportionality constant.

The free energy of a superconductor is now made up of two contributions: the electromagnetic field energy

$$F_{em} = \frac{1}{8\pi} \int \left( \bar{H}^2 + \bar{E}^2 \right) dV$$

(2.22)

and the contribution from the metal in the normal state and the surface energy as also described in equation (2.3).
2.2. BARDEEN-COOPER-SCHRIEFFER (BCS) THEORY

\[ F_{sc} = F_0 + \int \left[ \alpha |\psi|^2 + \frac{1}{2} \beta |\psi|^4 + \frac{1}{2m} \left( -i\hbar \vec{\nabla} - \frac{2q_e}{c} \vec{A} \right) |\psi|^2 \right] dV \]  

(2.23)

where the units have been changed to the cgs-system in order to yield convenient prefactors. The contributions described by equations (2.22) and (2.23) are now put into equation (2.21). Without going through the details of the following calculation, only the result in the form it will be used later on is given here:

The Ginzburg-Landau equations (2.6) and (2.7) take the form

\[ u \left( \frac{\partial}{\partial t} + i\mu \right) \psi = \left( \vec{\nabla} - 2i\vec{A} \right) \psi + \left( 1 - |\psi|^2 \right) \psi \]  

(2.24)

and

\[ \vec{j} = |\psi|^2 \left( \vec{\nabla} \arg \psi - 2\vec{A} \right) \]  

(2.25)

together with

\[ \vec{\nabla} \cdot \vec{j} = 0 \]  

(2.26)

\[ \vec{\nabla} \cdot \vec{A} = 0 \]  

(2.27)

where \( u \) is a parameter to be derived from microscopic theory.

2.2 Bardeen-Cooper-Schrieffer (BCS) Theory

2.2.1 Introduction

The Bardeen-Cooper-Schrieffer (BCS) theory describes how a microscopic mechanism, i.e. a mechanism occurring on the particle level, accounts for the phenomenon of superconductivity. Its basic concept is the assumption of an attractive force between the charge carriers that gives rise to a pairing of the carriers in so-called Cooper pairs and thus to a new quantum state that is energetically favoured at low temperatures.

As the detailed calculation is largely extended, only the most important results shall be quoted here. The theory was first published in [11], the account given here once again follows the representation in [95].

2.2.2 Cooper Pairs

The basic assumption of the BCS theory is a pairing of two charge carriers by an attractive force between the two of them. Such a pair of carriers is called a Cooper pair. In usual metals, the carriers will be electrons. The attractive force is described by a potential \( V \).

In "simple" metals, the pairing force is provided by a phononic interaction via the ions. But this is not necessarily always the case. The only prerequisite to be fulfilled is that the force must be attractive.

Cooper showed [20] that for a simplified potential of the form
CHAPTER 2. THEORIES ON SUPERCONDUCTIVITY

\[ V_0 = \begin{cases} -V, & \text{if } |\epsilon, \epsilon'| < \hbar \omega_D \\ 0, & \text{otherwise} \end{cases} \]  

(2.28)

where \( \omega_D \) is the Debye frequency of the system and the \( \epsilon, \epsilon' \) are the energies of the pairing electrons with respect to the Fermi level respectively, always a bound state with binding energy

\[ E_{\text{bound}} = 2\hbar \omega_D \exp \left[-\frac{2}{N(0)V}\right] \]  

(2.29)

exists, where \( N(0) \) is the electron density of states at the Fermi level.

2.2.3 The BCS Ground State

In order to understand the general behaviour of a many-electron system with attractive force between the electrons the ground state energy of a system of paired electrons as described before is calculated.

The detailed calculation involves second quantization methods and is quite lengthy, so only the result shall be given here. The calculation itself can be found in [11] as well as in many standard textbooks on superconductivity.

It turns out that the ground state energy of such a system \( E_0 \) differs from the ground state energy of a corresponding system in normal state \( E_N \) by

\[ E_0 - E_N = -\frac{2N(0)(\hbar \omega_D)^2}{\left[\exp(2/N(0)V)\right] - 1}. \]  

(2.30)

If \( E_0 - E_N \) becomes negative, the pairing state is energetically favoured compared to the normal state. This is mainly influenced by the temperature of the system and an external magnetic field the system may be subject to.

2.2.4 Collective Ground State

The two electrons paired up in a Cooper pair must have spins opposing one another in order to fulfill the Pauli principle. Thus, the total resulting spin of a Cooper pair is zero and hence it is a boson. Being a boson, the Cooper pairs themselves are not subject to the Pauli principle and an infinite number of them can occupy the lowest possible energy level. The BCS ground state is thus a collective quantum state in which all Cooper pairs are condensed and rigidly phase coupled.

2.2.5 The Energy Gap

The disappearance of the electrical resistivity can now be understood as a result of the electron system being in a collective quantum state. To get one electron out of it, a certain amount of energy must be used. If in a scattering process this energy can not be transferred to the electron, the scattering process cannot occur anymore. The existence of such an energy limit is described by an excitation gap \( \Delta \). No energy \( E < \Delta \) can take one electron out of the collective state, consequently all excited states are to be excited with energies \( E > \Delta \).
2.2.6 Excited States

Excited states are created by breaking up a Cooper pair. At zero temperature, the following density of states for these quasiparticles is obtained:

$$N(E) = \begin{cases} 0; & |E| < |\Delta| \\ \frac{N(0)|E|}{(E^2 - |\Delta|^2)^{1/2}}; & |E| > |\Delta| \end{cases}$$

(2.31)

Here, $N(0)$ denotes the density of states of normal conducting electrons at the Fermi edge and $\Delta$ is the excitation gap.

For a finite temperature, an energy distribution function of the form of the Fermi-Dirac distribution is found. The system of excited quasiparticles can thus be regarded as a system of fermions. Tinkham [96] emphasises that the fact of having a system with a bosonic ground state but fermionic excited states disqualifies a superconductor from being regarded as an example of a Bose-Einstein condensate. To have the latter, it is necessary to have a bosonic ground state and bosonic excited states.

Regarding the temperature dependence of the excitation gap $\Delta$ and especially the fact that $\Delta \to 0$ for $T \to T_c$ yields the following implicit expression for the critical temperature can be obtained:

$$1 = N(0)V \int_0^{\hbar \omega_D} \epsilon^{-1} \tanh \left( \frac{\epsilon}{2k_BT_c} \right) d\epsilon.$$  

(2.32)

In the special case of weak coupling $N(0)V << 1$, this can be approximated by:

$$k_BT_c = 1.14 \hbar \omega_D \exp \left[ -1/N(0)V \right]$$

(2.33)

which again can be rewritten as

$$2\Delta(0) = 3.52k_BT_c$$

(2.34)

with $\Delta(0)$ the so-called energy gap of the superconducting system.
Part III

Experimental Results and Discussion
Chapter 3

Methods

3.1 Magnets

The magnetic fields used in the experiments were generated by a variety of facilities of the Grenoble High Magnetic Field Laboratory. Mainly two kinds of magnet systems were used: resistive magnets in which electric power is dissipated and has to be removed in the form of heat and a superconducting magnet, through which the current passes dissipationlessly.

3.1.1 Resistive Magnets

Generalities

A resistive electromagnet has the disadvantage of producing large amounts of heat at high fields due to power dissipation in the coils. The heat is usually removed by cooling water pressed directly through the coils. This provides an efficient heat removal, but may represent an additional source of noise as the water flow may cause some mechanical vibration of the magnet itself.

These disadvantages are however counterbalanced by a less strict limitation in the maximum field. In principle, there is no upper limit for a maximum field produced by this technique. The limitations are more of a practical nature: mechanical stresses due to Lorentz forces in the magnet and effective cooling. Regarding the latter, the efforts that must be made to remove the heat increase roughly with the square of the maximum field, which represents a technical hindrance to further increasing an already high field.

Moreover, the heat has to be dispersed in a volume large enough to avoid reaching critical temperatures anywhere, especially the boiling point of the cooling water. Nevertheless, this technique principally allows one to reach arbitrary high fields, but then also imposes arbitrary large magnets and arbitrary power and cooling needs.

However, the maximum reachable fields in practise are nowadays in the range of 30T for continuous fields which is well above the state-of-the-art technology for superconducting magnets (about 20T).

A normal conducting, dissipative magnet is therefore to be favored for experiments in which it is desirable to have a field as high as possible without noise restrictions and homogeneity demands being too excessive.

For completeness, it should also be mentioned that dissipative magnets allow for a
faster change rate of the fields than superconducting magnets. Whether this represents an advantage or not, depends very much on the actual experiment. The production of fields being higher than those of dissipative magnets can be done by combining superconducting and normal conducting coils in a so-called hybrid magnet.

**Kinds of Coils**

In the Grenoble High Magnetic Field Laboratory, two different kinds of coils are used, so-called *Bitter coils* and *polyhelix coils*.

The former follow a construction principle first described by F. Bitter [14], who stacked copper discs on top of each other. Slitted insulating sheets between the copper discs are arranged in such a way that the electrical current passes helically through the construction. Vertically drilled holes through the whole construction allow for passing of the cooling water that can provide a very efficient cooling.

Bitter magnets are relatively easy to build, are mechanically stable and robust and easy to cool efficiently. However, they are restricted by their design to a specific geometry for the electrical current in the whole magnet volume. This latter circumstance represents a disadvantage in optimising a coil in such a way that for a given volume and maximum heat dissipation a maximum magnetic field can be produced.

This disadvantage is overcome by the polyhelix coil [112], basically made up of a tube from which material is cut away along a helicodial line, in most cases by spark erosion. This technique allows for variations of the conductor’s thickness and inclination as a function of the positions. Thus, additional degrees of freedom that can be varied in an optimisation process are provided and enables this type of coil to produce considerably higher magnetic fields per electric power and magnet volume than a Bitter magnet. Polyhelix coils are, nevertheless, considerably more difficult to calculate and to produce than Bitter coils.

For the experiments described in this work, the following resistive magnets of the Grenoble High Magnetic Field Laboratory were used:

**M6**

The magnet M6 is a Bitter magnet with polyhelix insert producing a maximum field of 23T at a nominal electric power dissipation of 10 MW. The bore diameter is 50mm.

**M9/M10**

The magnets M9/M10 also consists of an outer Bitter magnet with a polyhelix insert. It produces a maximum field of 28T under standard conditions. On special demand, the maximum field can be risen to 30T. The nominal power consumption of this magnet is 20MW and its bore diametre depends on the inset. In the configuration used for the experiments described in this work, an insert providing a room temperature bore of 50mm diameter was used. Further technical details about the construction of this magnet can be found in [9].
3.2. TORQUE METHOD TO MEASURE MAGNETISATION

3.1.2 Superconducting Magnet

In comparison with a resistive magnet, the main advantage of a superconducting magnet is the absence of dissipation of large amounts of electrical power, so that neither the provision nor the removal of that power is necessary. There is however the need for cryogenics at temperatures of liquid Helium ($\leq 4.2K$) to maintain the superconducting state of the coil.

Superconducting magnets are limited in their maximum fields by the existence of the critical field $H_{c2}$ passing of which would destroy the superconducting state and thus restoring the normal conducting state with the coil becoming resistive and therefore dissipating power. To prevent this, the field of the magnet has to be kept below $H_{c2}$ of the coil material at the operation temperature. Nowadays, superconducting magnets up to about 20T are available.

Due to the dissipationless conduction in the coil, every change of field implies in important current in the coil that cannot be dissipated in the coil itself. Therefore, it must be dissipated in the normal conducting supply leads and in the power supply. Consequently, this situation of a large self-inductance, requires slow change rates of the magnetic field.

Moreover, the stability of the supercurrent in the coil provides for a very good spatial and temporal homogeneity of the field produced. Additionally, the absence of water cooling removes one of the potential noise sources in resistive magnets.

A superconducting magnet is therefore desirable for experiments requiring very high standards for the noise level and the homogeneity of the field, without demanding for too high a maximum field.

Superconducting magnet used in this work

The superconducting magnet used for the experiments described in this work has been supplied by Oxford Instruments under the project number 30994. It has a 60mm diameter room temperature bore. Its maximum fields are 10.25T at 4.2K and 2.2K when the $^4$He bath is pumped to a temperature of 2.2K.

3.2 Torque Method to Measure Magnetisation

3.2.1 Principles

One of the principal variables studied in the experiments described in this work is the magnetisation of the sample. The measurements are carried out using the torque method being developed for this purpose by Christ and Biberacher [18] [19].

The principal experimental setup is sketched in figures 3.1 and 3.2. A leaf spring carries the sample and constitutes one plate of a capacitor. The other plate of the capacitor is made up by an electrode in the ground plate of the system.

If now the sample exhibits a magnetisation $\vec{M}$ when it is exposed to an external magnetic field $\vec{B}$, a torque $\vec{\tau}$ proportional to the magnetic moment is created as the sample tries to align itself in such an orientation as to minimise its energy in the field:

$$\vec{\tau} = \vec{M} \times \vec{B}. \quad (3.1)$$

This results in a deformation of the leaf spring and thus in a change of the capacitance of the capacitor made up by the spring and the counter electrode. This change in capacitance
is detected by means of a balanced capacitance bridge the debalancing signal of which is detected by means of a lock-in amplifier. Typical operation frequencies are in the range of 5 kHz, typical capacitances of the set-up are in the range of 1...2 pF.

It can be seen from equation (3.1) that it is necessary to have a component of $\vec{M}$ not being parallel to $\vec{B}$ to detect anything with this method. Taking into account equation (1.12), equation (3.1) can be rewritten for the modulus of $\vec{r}$

$$\tau = -\frac{1}{F} \frac{dF}{d\theta} M_{\text{osc}} B$$

(3.2)

by which it can be seen that there must be some anisotropy, i.e. some dependence of the cross-sectional area of the Fermi surface proportional to the oscillating frequency $F$ to have $\vec{r} \neq 0$.

### 3.2.2 Torque Interaction

Torque interaction is an artefact that can occur in magnetooscillation measurements using the described torque method. Its origin is the displacement of the sample in the field. Generally, the observed oscillation frequency depends on the orientation of the sample with respect to the external magnetic field. The displacement implies a change of the sample orientation and thus a modification of the oscillation frequency spectrum. In case of small movements of the magnetometer, this effect is negligible, can however become important if the deformation of the leaf spring becomes important.

In the case of important torque interaction torque signal $T = T_0 \sin(2\pi F/B)$ is thus subject to a periodic modification of the oscillation frequency $F$ by an amount $\partial F/\partial \theta$, mediated by the torque $T$ and the spring constant $\eta = \partial \theta / \partial T$:

$$T = T_0 \sin \left( \frac{2\pi F}{B} + \frac{2\pi}{B} \frac{\partial F}{\partial \theta} \eta T \right).$$

(3.3)

The torque interaction is negligible if the non-linear term in (3.3) is small, i.e.

$$\frac{\partial F}{\partial \theta} \eta T \ll 1.$$  

(3.4)

If torque interaction is considerable, the non-linear term in (3.3) yields modifications of the harmonic spectrum of $F$ that do not originate from the system itself and must therefore be regarded as an artefact.

In the case of several frequencies present in the spectrum, the total torque is given by

$$T = \sum_{\alpha} T_{0\alpha} \sin \left( \frac{2\pi F_{\alpha}}{B} + \frac{2\pi}{B} \frac{\partial F_{\alpha}}{\partial \theta} \eta T \right).$$

(3.5)

Note that although each frequency has its individual term in (3.5), each of these non-linear terms contains the total torque $T$, which contains all the frequencies present. It is via this interaction that the artificial combination frequencies are created by these non-linear terms.
Figure 3.1: Schematic sketch of the leaf spring torque magnetometer. The leads used to carry out a simultaneous resistivity measurement in some of the experiments are also shown.
Figure 3.2: Schematic sketch of the electrical circuit used to measure the capacitance of the leaf spring torque magnetometer. The magnetometer itself is situated inside the cryostat which itself is located in the magnet bore. Cryostat and magnet are not shown in this sketch.
3.3. Measurements of Electrical Resistivity

Another important parameter being observed in the context of this work is the electrical resistivity. The measuring circuit being used is sketched in figure 3.4.

The sample is contacted at four points. Through two of them, a current is passed while the other two ones are used to detect the voltage drop caused by the resistivity of the sample. The voltage is detected using a lock-in amplifier. Before being detected, the signal is passed through a low-noise signal transformer to provide for impedance matching.

The frequencies were kept relatively low ($\leq 300$ Hz) to ensure quasi-DC measuring conditions. On the other hand, it was desirable to keep off the mains frequency and its harmonics.

The current is generated using a signal generator. It is limited by a high-ohmic pre-resistor $R_1$, a low-ohmic pre-resistor $R_2$ was used in some measurements to adjust the phase of the lock-in amplifier before the actual measurement on the sample was started.

The adjustment procedure was as follows: first, the sample was disconnected from the input of the lock-in amplifier and the latter was connected parallely to $R_2$. Then, the phase of the lock-in was tuned in such a way that the measured voltage in the X channel of the lock-in was maximized. Then, $R_2$ was disconnected from the lock-in amplifier input and the sample was re-connected to it. This procedure ensures to see exclusively ohmic contributions to the signal in the X channel of the lock-in, whereas all non-ohmic contributions appear in the Y channel.
Figure 3.4: Electrical circuit as used to measure resistivity. The switches and $R_2$ serve to adjust the phase of the lock-in amplifier in such a way that ohmic and non-ohmic contributions to the signal are separated, for details about the procedure, see main text.
3.3. MEASUREMENTS OF ELECTRICAL RESISTIVITY

The contacts on the sample were made using carbon conducting paste with contact resistances of 10...50 Ω per contact, depending on the actual quality of the contact.

In the experiments described in this work, the electrical resistivity was measured simultaneously to the torque caused by the magnetisation. For this purpose, the sample was put on the leaf spring and at the same time contacted by means of four thermally treated gold wires of 12 μm diameter as shown in figure 3.1.
Chapter 4

Organic Conductors and Superconductors

This section summarises some of the main and relevant properties of organic metals and superconductors that constitute the object of a large part of the experimental investigations described in this work. An extensive review on these matters is [45].

4.1 Origin of Conductivity, Charge Transfer

While the large majority of organic compounds are electrical insulators, there is a number of compounds that are electrical conductors. These are referred to as organic conductors and, if they exhibit superconductivity, as organic superconductors.

They usually consist of an organic cation molecule and an anion molecule that is usually anorganic. Nevertheless, there are examples of organic conductors possessing an organic anion.

Their conductivity is caused by a transfer of electronic charge from the anion molecules to the cation molecules. Thus, the latter acquire an excess charge that carries the electrical current. Consequently, conduction occurs only in the cation molecules, the anion molecules do not carry any current because they do not possess any moveable charges.

The first observation of electronic conductivity in an organic compound dates back to the 1960s and was done on a semiconducting compound [44]. The research in this field was greatly encouraged by a hypothesis published by Little in 1964 [65] predicting that organic conductors could favour excessive superconducting transition temperatures. He imagined a mechanism for the Cooper pairing necessary to yield superconductivity in which the attractive force between two electrons should not be mediated by a relatively heavy lattice ion but by the positive charge created by the displacement of an electron. As the mass of the electron is much smaller than that of an ion, this mechanism was thought to provide a stronger attractive force between the pairing electrons than that yielded by the standard BCS-mechanism.

However, so far neither the described mechanism of superconductivity nor the excessive superconducting transition temperatures as predicted by Little have been found. In addition, the mechanism of superconductivity occurring in the organic superconductors is not yet understood either, e.g. [113][114].
4.2 Cation Molecules

Organic conductors have been synthesised using different cation molecules. All compounds investigated in the context of this work are based on the cation molecule bisethylenedithio-tetrathiafulvalene, which will be subsequently referred to as BEDT-TTF or ET. A structure of the molecule is shown in figure 4.1.

4.3 Anisotropy and Low Dimensionality

As mentioned before, the conductivity is produced by the transfer of charges from the anions to the cations, and consequently occurs in the cations only. As the crystal structure leads to an anisotropic distribution of anions and cations, the conductivity tensor of such a crystal is anisotropic as well. As an example, figure 4.2 shows the crystal structure of $\kappa$-(ET)$_2$Cu(NCS)$_2$. It can be seen that planes of anion and cation molecules are stacked one on another. Consequently, the conductivity parallel to the planes is much higher than perpendicular to them. To a good approximation, the electronic transport is confined to the two dimensions parallel to the sheets. Thus, the dimensionality of the electronic system has been reduced. There are one-dimensional systems as well, but as they are not investigated in this work, there are not discussed further here.

4.4 Deviations from Perfect Low Dimensionality, Warping, Beating

Although the electronic motion is confined to the cation planes, in many cases there is some residual interaction between the conducting cation planes across the anion planes that leads to deviations from exact two-dimensionality of the electronic system.

As far as the electronic properties in $\vec{k}$-space are concerned, the Fermi surface of a perfectly two-dimensional system of free electrons is a cylinder. Residual interaction between the conducting planes now results in deviations from the exact cylindrical shape of the Fermi surface, an effect known as warping. This is illustrated in figure 4.3.

A model for warping that is employed very often is a cosine-modulated cylinder:

$$E_{n,k_z} = \hbar \omega_c (n + 1/2) - 2t \cos(k_z d).$$  \hspace{1cm} (4.1)

Here, $d$ is the thickness of one conducting layer and $t$ is called the transfer integral. The transfer integral is a measure of the degree of the warping.

A system exhibiting significant warping is said to be quasi two-dimensional.
4.4. DEVIATIONS FROM PERFECT LOW DIMENSIONALITY, WARPing, BEATING

Figure 4.2: Crystal structure of $\kappa$-(ET)$_2$Cu(NCS)$_2$ showing the altering stacking of conducting cation and non-conducting anion planes that lead to the anisotropy of the conductivity tensor and the low-dimensionality of the electronic system. From [97].

Figure 4.3: Illustration of the warped Fermi surface of a quasi two-dimensional conductor: interactions between the conducting layers result in deviations of the shape of the Fermi surface from the exact cylindrical shape of a perfectly two-dimensional electron system.
In the context of magneto-quantum oscillations, warping leads to the appearance of two frequencies in the magneto-quantum oscillation spectrum, one corresponding to the maximum and the other to the minimum diameter of the warped cylinder. Their mutual interference leads to the appearance of beating nodes in the observed quantum oscillations.

Considering two quantum oscillation frequencies centered around \( F \) and differing by \( \Delta F \) for the oscillating part of equation (1.11) gives

\[
M_{\text{osc}} \propto \sin \left(2\pi \left(F + \frac{\Delta F}{2}\right)/B - \frac{\pi}{4} + \gamma_M\right) + \sin \left(2\pi \left(F - \frac{\Delta F}{2}\right)/B + \frac{\pi}{4} + \gamma_M\right) \quad (4.2)
\]

\[
= \cos \left(\pi \Delta F/B - \frac{\pi}{4}\right) \sin \left(\pi F/B + \gamma_M\right) \quad (4.3)
\]

using addition theorems. The node positions can now be found by finding the zeroes of the leading cos-term in equation (4.3) resulting in

\[
B_n = \frac{4}{4n + 3} \Delta F \quad (4.4)
\]

with \( n = 0, 1, 2, 3, \ldots \).

4.5 Nomenclature

The usual nomenclature of organic conductors is made up of three parts: first comes a Greek letter designating the crystal structure. This refers especially to the positions of the cation molecules one with respect to another. Second, the cation is designated either by its exact chemical formula or by an abbreviation. Third and last is the designation of the anion, usually by its chemical formula.
Chapter 5

Beating Effects and Phase Relations in \( \beta-(\text{BEDT-TTF})_2\text{IBr}_2 \)

5.1 Motivation

The initial motivation for the experimental studies described in this chapter was the observation that in simultaneous observations of the de Haas-van Alphen (dHvA) effect and the Shubnikov-de Haas (SdH) effect in a quasi-two-dimensional organic metal the beating nodes that are due to the Fermi surface warping do not occur at the same field values as it is expected from Lifshitz-Kosevich theory. The effect was first noted in simultaneous measurements on the system \( \kappa-(\text{ET})_2\text{Cu[N(CN)]}_2\text{Br} \) by H. Weiss et al. \cite{109,110}. The effect was also observed in the compound \((\text{ET})_4\text{[Ni(dto)]}_2 \) \cite{81}. It should however be noted that the experimental results reported in \cite{81} were not obtained by a simultaneous measurement of the two effects.

The results reported in \cite{109} and \cite{110} lack from the fact that there is only one node visible in the accessible field range. Thus, it was of interest to examine the effect on a system whose beat frequency \( \Delta F \) provides a sufficient number of nodes between the minimum field \( a \) which oscillations become visible and the highest available field. The compound \( \beta-(\text{ET})_2\text{IBr}_2 \) exhibits beating frequencies of up to about 50T, depending on the tilting angle with respect to the magnetic field and was thus chosen for a systematic study of the phenomenon.

5.2 Description of the System

The compound \( \beta-(\text{ET})_2\text{IBr}_2 \) has a pronounced warping of the Fermi surface with a frequency difference of up to about 50T - see figure 5.1. A theoretical Fermi surface model has been calculated by H. Kübler et al., the main features of the resulting Fermi surface are shown in figure 5.2.

A "second set of nodes" as claimed by Wosnitza et al. (\cite{113} and references therein) was neither seen by other groups (e.g. \cite{52}), nor in the context of the present work.

The samples used in the present work were synthesised by N.D. Kushch.
Figure 5.1: Angular dependence of the beating frequency $\Delta F$ in $\beta-(ET)_2IBr_2$. From [113].

Figure 5.2: Model of the Fermi surface of $\beta-(ET)_2IBr_2$ by Kübler et al. [60]. The solid line represents the intersection with the plane $k_c = 0$, the dashed line with $k_c = 0.25$ and the dotted one with $k_c = 0.5$. 
5.3 Importance of Measuring the Two Effects Simultaneously

It should be stressed that it is important to measure the two effects simultaneously on one and the same sample in order to obtain data that allow analysis for the effect in question. The Lifshitz-Kosevich theory gives the position of the $n$th node on a field scale $B$ as follows: $B_n = 4/(4n + 3)\Delta F$ with $n = 0, 1, 2, \ldots$. The node position is thus proportional to the beating frequency $\Delta F$ by a factor that practically ranges from about 1/10 to 1.

Looking at figure 5.1, it can be seen that due to the strong dependence of $\Delta F$ on the tilting angle angular shifts of less than a degree may be sufficient to shift a node by as much as 1T. Such a shift can however easily be inflicted to the experimental set up if it has to be warmed up, re-arranged for measuring the other effect and re-cooled. Thus, the simultaneous measurement of magnetisation and resistance is of crucial importance for the observation of the phenomena to be regarded here.

For all the experimental results described in the following section, the sample was thus mounted on the spring leaf and gold or platinium wires of 12µm thickness provided electric contact with the sample without damping the movement of the spring leaf too much.

5.4 Experimental Results

The experimental data up to 14T presented and discussed here have been obtained at the Walther-Meissner Institute in Garching / Germany. Their analysis has been done in the framework of this thesis. The data up to 23T have been obtained in experiments at the Grenoble High Magnetic Field Laboratory.

5.4.1 Characterisation of the Used Sample

The extraction of characterising parameters such as the Dingle temperature $T_D$ and the effective masses both relies on the analysis of the quantum oscillation amplitudes. In the case of a quasi-two dimensional system with a significant beating, the occurrence of the beating is a serious hindrance in such an analysis. Thus, magnetic field and temperature dependent measurements of the oscillation amplitudes were done at the zero beating angles, where only one frequency occurs in the quantum oscillation spectrum. The analysis procedures are the same as described in the chapter on $\kappa$-(ET)$_2$Cu(NCS)$_2$.

The effective electron mass was extracted from temperature dependent measurements of the de Haas-van Alphen amplitude at -19.2° tilting angle. Extrapolated to the zero degree position - i.e. planes of the sample perpendicular to the magnetic field - the dHvA data gives $4.08 \, m_e$ and the SdH data $3.96 \, m_e$. These values have been used for fitting the Dingle temperature for both sets of data - dHvA and SdH - separately. The data used for the Dingle plot have been taken at the beating zero at 32.34°. The Dingle plots are shown in figures 5.3 and 5.4. The analysis was made for a sample temperature of 0.56K. This temperature considers the heating of the sample by the current passing through it to measure its resistivity. The bath temperature was 0.46K. The sample temperature of 0.56K has been determined by comparing the observed dHvA amplitude to dHvA amplitudes recorded on the same sample with the same set up at different bath temperatures but without current passing through the sample.
BEATING AND PHASE IN $\beta - (BEDT - TTF)_2IBr_2$

Figure 5.3: Dingle plot for the dHvA amplitude at 32.34° tilting angle. Only the apparently straight part as shown in the graph was used for the analysis.

Figure 5.4: Dingle plot for the SdH amplitude at 32.34° tilting angle. Only the apparently straight part as shown in the graph was used for analysis.
5.4. EXPERIMENTAL RESULTS

Both Dingle are not exactly straight lines as expected. This probably indicates a slight misalignment of the sample, resulting in some residual beating that was not obvious during the measurements. However, the straight line fits yield basically the same value for \( T_D \) if only the apparent straight line part in the middle of the field range is considered for the dHvA oscillation. For the SdH oscillation, the Dingle plot is closer to a straight line and the whole set of data was used. In this way, the Dingle temperature of the used sample is determined to be 360mK.

5.4.2 Method of Analysis

The observed quantum oscillations have been plotted as function of the inverse magnetic field. Then, a grid with the period length as line distance has been superimposed to the plot. The node positions have been read by comparing the relative positions of the minima and maxima of the oscillation to this grid. In this way, the phase shift occurring at each node was made visible and used for making out the node positions.

5.4.3 Node Positions

The nodes observed do clearly not occur at the same field values for the dHvA oscillations and the SdH oscillations. A summary of the observed node positions as function of the sample’s tilting angle with respect to the magnetic field is shown in figure 5.5. For the measuring of the tilting angle, the orientation of the magnetic field being perpendicular to the conducting planes is defined as zero.

The nodes are indexed according to the following convention:

Supposing 1/\( B \)-periodicity of the node positions, a straight line was fitted to the node positions as a function of integer numbers in such a way that it includes the node positions as well as the origin of co-ordinates. Then, beginning at the low value end of the 1/\( B \)-axis, the nodes have been enumerated beginning with 0. The number 0 is thus associated with the node the appears as the last one when increasing the field. In such a way, the obtained indices are consistent with those used in equation (4.4).

5.4.4 Phase Shifts

The observed node positions shown in figure 5.5 have been converted to phase shifts in the following way: the distance of two dHvA nodes on a 1/B scale was taken as half the period length, thus, distance between two dHvA nodes corresponds to a phase of \( \pi \). The position of the SdH nodes is expressed as the distance between itself and the corresponding dHvA nodes (dHvA node of the same index) and this related to the period as determined from the two bracketing dHvA nodes:

\[
\Delta \phi = \pi \frac{(B_{n_{dHvA}}^{dHvA})^{-1} - (B_{n_{SdH}}^{dHvA})^{-1}}{(B_{n_{dHvA}}^{-1}) - (B_{n_{dHvA}^{-1}}^{-1})}.
\]

(5.1)

Thus, the positions of the SdH nodes are given as phase shifts with respect to the period of the beating oscillation. At angles where only one dHvA node was visible, the beat period was estimated by extrapolating the positions of the unobserveable nodes using the so-called ”Yamaji’s law”[118][113]:
Figure 5.5: Positions of the observed nodes in the dHvA and SdH oscillations of $\beta-(BEDT-TTF)_2IBr_2$ as a function of the sample’s tilting angle with respect to the magnetic field. The node positions are given on an inverse magnetic field scale.
5.4. EXPERIMENTAL RESULTS

Figure 5.6: Relative shifts between the beating nodes of the dHvA and SdH oscillations in $\beta$-(ET)$_2$IBr$_2$ as function of the tilting angle with respect to the magnetic field. Shifts without error bars are obtained using extrapolation methods described in the main text.

\[
\Delta F \cos \theta = \Delta F_{\text{max}} J_0 (c' k_F \tan \theta - a)
\] (5.2)

where $c'$ is the interlayer distance and $a$ a parameter describing the azimuthal asymmetry. Here and also in subsequent sections, $J_n$ is the Bessel function of nth order. In the interpolation, $c'$ was estimated by the room temperature crystallographic value 15.093 Å[113] and the Fermi wave vector by $k_F = \sqrt{2 q_e F_{\text{av}} / \hbar}$ with $F_{\text{av}}$ the average of the two interfering quantum oscillation frequencies. The angles at which two dHvA nodes could be observed where used to obtain appropriate fitting parameters which then where used to determine $\Delta F$ for angles where only one dHvA node could be observed. This procedure was applied in the angular range from $\theta = 23.5^\circ$...26°

5.4.5 Angular Range from 12.5° to 24°

In this angular range, two to three SdH nodes could be observed within the field range up to 14T. A tendency for an increasing of the phase shift with increasing angle is visible, although not very pronounced for angles up to 19°, where it is within the error limits.
The increase becomes steeper at angles $\theta > 19^\circ$. In most cases, the shifts corresponding to nodes with smaller indices have the higher shift than those with higher indices, in other words, at constant angle, the shift seems to increase with increasing magnetic field. There is only two exceptions from that general observation within this field range, it is the points at $17.7^\circ$ and the one at $18.9^\circ$. It should however be noted that in this whole angular range the shift values overlap within the error bars.

5.4.6 Angular Range from 24° to 26.5°

In this range, the increase of the shift with the magnetic field becomes much more pronounced than at lower angles. Since only one dHvA node could be observed in this angular region, the extrapolating procedure using Yamaji’s law as described above has been applied.

5.4.7 Angular Range from 26.5° to 28.5°

In spite of the apparently smooth beginning of the curve as shown in figure 5.5, there is an apparent jump towards lower shifts here. It must however be noted that especially in this region the obtained phase shift is uncertain. Only one dHvA node is observed within the field range, at fields where the amplitude is already quite low, resulting in a low signal to noise ration which makes it very difficult to exactly localise the node position. In addition to this uncertainty, the beat frequency can only be estimated by extrapolation.

5.4.8 Angular Range from 28.5° to 30°

The trend to higher values with increasing angle is continued, with the extreme consequence of a phase shift bigger than $\pi$. Although the beat period can only be obtained by extrapolation, this extreme value is surely not an artefact due to the extrapolation process, since figure 5.5 shows clearly a crossover of the SdH1 node positions as function of the angle over the dHvA0 series. Under this aspect, it should also be noted that the SdH1 series shows a tendency to do the same in the same angular range. But, as it has been said in the previous subsection, the base for an extrapolation is particularly weak in this range, an extrapolation did not appear to make sense here and so it cannot be said with certainty if the SdH1 series shows the same kind of crossover behaviour.

5.5 Results at High Magnetic Field

Another sample of the same compound was examined in the described way in the M6 magnet of the Grenoble High Magnetic Field Laboratory, allowing to achieve maximum fields of 23T. This sample, however, showed a bad signal-to-noise ratio in the resistance measurement since it was relatively broad and flat, resulting in generally low resistance values. Because of this, only limited data could be obtained and the exact position of the SdH node is quite uncertain. It was only possible to observe one SdH node at high field, bracketed by two adjacent dHvA nodes at three angles. The observed node positions and their corresponding phase shifts are listed in table 5.1. With an estimation of the error on the shift using the Gaussian method starting with estimates of the uncertainty in reading the nodes from the raw data, the error of the said shifts is estimated as $0.07\pi$. 

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**BEATING AND PHASE IN $\beta-(BEDT-TTF)_{2}IBr_{2}$**


5.6. GENERAL REMARKS

<table>
<thead>
<tr>
<th>Angle / deg.</th>
<th>dHvA0</th>
<th>SdH1</th>
<th>dHvA1</th>
<th>ΔF/T</th>
<th>Shift/π</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.8</td>
<td>20.92</td>
<td>17.95</td>
<td>13.33</td>
<td>36.64</td>
<td>0.71</td>
</tr>
<tr>
<td>19.2</td>
<td>20.73</td>
<td>18.7</td>
<td>13.28</td>
<td>36.4</td>
<td>0.79</td>
</tr>
<tr>
<td>20.7</td>
<td>19.19</td>
<td>17.44</td>
<td>12.51</td>
<td>33.99</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 5.1: Observed node positions and relative shifts at high fields. The error of the shift is estimated to be about 0.07π.

5.6 General Remarks

The first and most evident result is the observation that the beating nodes in the SdH and dHvA oscillations do not appear at the same field values as it can be expected from the Lifshitz-Kosevich and Adams-Holstein theories - for details about how this expectation arises, see the next section. The most spectacular result is surely the observed phase shift bigger than π for at angles close to 30°. As it can be seen from figure 5.1, the dHvA oscillations of this compound exhibit a zero of the beating at about 32°. It can therefore be speculated that the occurrence of this beat zero somehow implies the increase of the shift. At this angle, warping of the Fermi surface does practically not play a role anymore, minimum and maximum orbit have the same diameter, there is only one extremal orbit and consequently only one oscillation frequency and no beating anymore. Thus, it might also be thought of as of an increase of the two-dimensional character of the system when approaching the angles of zero beating frequency. One could say that with increasing the two-dimensional character of the system, the deviation from the Lifshitz-Kosevich / Adams-Holstein theories is increased. Since these theories describe well the three-dimensional case, it would seem logical that they represent worse and worse approximations of the system whose two-dimensional character becomes stronger. A more detailed discussion within the context of some established and some new theoretical ideas is given in the next section.

It should also be noted that in spite of the still considerable error on the finally determined phase shifts, the measurement itself was done with quite a good accuracy. Most nodes positions could be determined with an accuracy of less than a period length on the B-scale. However, the sensitivity of the phase shift as defined by equation (5.1) is considerable so that even the obtained accuracy leads to a considerable total error. Naturally, this effect becomes much more important for the high field measurements where for the reasons already mentioned the SdH node positions could only be determined with a considerable uncertainty.

5.7 Comparison with Theoretical Models

5.7.1 Generalities

The experimental evidence presented in this chapter shows that this system - and the others in which the effect has been observed - cannot be explained within the Lifshitz-Kosevich and Adams-Holstein theories. Within these theories, the oscillations of the magnetisation and the resistance are described by sin and cos terms respectively (c.f. equations (1.11) and (1.28) with the same phase factors. This means that within Lifshitz-
Kosevich theory, two interfering oscillations with frequencies differing by $\Delta F$ are described by

$$M_{\text{osc}} \propto \sin \left( 2\pi \left( F + \Delta F/2 \right)/B - \pi/4 + \gamma_M \right) + \sin \left( 2\pi \left( F - \Delta F/2 \right)/B + \pi/4 + \gamma_M \right)$$

$$= \cos \left( \pi \Delta F/B - \pi/4 \right) \sin \left( \pi F/B + \gamma_M \right)$$ (5.3)

and analogously

$$\sigma_{\text{osc}} \propto \cos \left( 2\pi \left( F + \Delta F/2 \right)/B - \pi/4 + \gamma_\sigma \right) + \cos \left( 2\pi \left( F - \Delta F/2 \right)/B + \pi/4 + \gamma_\sigma \right)$$

$$= \cos \left( \pi \Delta F/B - \pi/4 \right) \cos \left( 2\pi F/B + \gamma_\sigma \right).$$ (5.4)

The envelope of the resulting oscillation is described by the first cos term in equations (5.4) and (5.6) which are identical, this means that the beating nodes in both kinds of quantum oscillations should appear at the same field. This is obviously not the case. It is worth noting that even if the Onsager shifts $\gamma_M$ and $\gamma_\sigma$ as appearing in equations (1.11) and (1.28) do not affect the beating shift even for the case $\gamma_M \neq \gamma_\sigma$.

The phase factors $\mp \pi/4$ appearing in the oscillating terms are due to an approximation in the derivation of the Lifshitz-Kosevich formula that makes use of the three-dimensionality of the examined system. As the system studied here is a quasi two-dimensional system, it is not a priori clear if this approximation holds. Indeed, it has been shown by Shoenberg and Templeton in [91] that non-fulfillment of this condition can lead to considerable deviations of the phase factors from $\mp \pi/4$. This, however, should hold for both effects in the same manner, so that in the result, the nodes should again appear at the same fields since both effects are supposed to be controlled by the same Fermi surface.

Therefore, a theoretical model to explain the observed phase shifts, must take into account more specific conditions than just the Fermi surface. One significant difference between the dHvA and the SdH effect is that the dHvA effect is determined by oscillations of the density of electron states at the Fermi edge only, the SdH oscillations are determined by two oscillatory effects: one is the said density of state oscillation, the other one is the oscillation of the velocities of electrons at the Fermi level as a consequence of the 2D-dispersion law. These latter become important when the cyclotron energy becomes comparable to the Fermi surface warping [40]. The competition of these two oscillations in the transport leads to the observed phase change of the SdH oscillation. Since the velocity does not play a role for the equilibrium dHvA effect, its phase remains unaffected.

### 5.7.2 Model by Grigoriev

Grigoriev et al. developed a model [33] that is based on the following idea: while the dHvA effect is determined by oscillations of the density of electron states at the Fermi edge only, the SdH oscillations are determined by two oscillatory effects: one is the said density of state oscillation, the other one is the oscillation of the velocities of electrons at the Fermi level as a consequence of the 2D-dispersion law. These latter become important when the cyclotron energy becomes comparable to the Fermi surface warping [40]. The competition of these two oscillations in the transport leads to the observed phase change of the SdH oscillation. Since the velocity does not play a role for the equilibrium dHvA effect, its phase remains unaffected.
5.7. COMPARISON WITH THEORETICAL MODELS

The authors first follow [17] to get an expression for the oscillatory magnetisation of a quasi two-dimensional model. Starting from the spectrum of a warped cylinder Fermi surface with cosine-modulation as described by (4.1).

They first calculate the density $g(E)$ of electron states at the Fermi edge by summing over all quantum numbers at fixed energy $E$:

$$g(E) = \sum_{n=0}^{\infty} \frac{N_{LL}}{\sqrt{4t^2 - (E - \hbar\omega_c(n + 1/2))^2}}$$  \hspace{1cm} (5.7)

where $N_{LL}$ is the Landau level degeneracy. Using the Poisson summation formula, they obtain (no higher harmonics considered):

$$g(E) \propto \cos(2\pi E/\hbar\omega_c) J_0(4\pi t/\hbar\omega_c).$$ \hspace{1cm} (5.8)

This yields the oscillatory part of the magnetisation as:

$$M_{osc} \propto \sin(2\pi E_F/\hbar\omega_c) J_0(4\pi t/\hbar\omega_c) R_T.$$ \hspace{1cm} (5.9)

For the electric resistivity, they start with the Boltzmann transport equation:

$$\sigma_{zz} = q^2 e I \tau$$ \hspace{1cm} (5.10)

where $\tau$ is the momentum relaxation time which is inversely proportional to the density of states at the Fermi edge. $I$ is the sum of all squared electron velocities at the Fermi level: $I = \sum_{E=E_F} |v_z|^2$. The velocities $v_z$ are expressed by:

$$v_z(E,n) = d/\hbar \sqrt{4t^2 - (E - \hbar\omega_c(n + 1/2))^2}$$ \hspace{1cm} (5.11)

with an index $n$ enumerating the Landau levels. As a result, they obtain:

$$I \propto \cos(2\pi E/\hbar\omega_c) J_1(4\pi t/\hbar\omega_c) R_T.$$ \hspace{1cm} (5.12)

Now, the case of large arguments of the Bessel functions in (5.9) is regarded. In this case, the Bessel functions can be approximated by trigonometric functions according to $J_0/1(x) \approx \sqrt{2\pi x} \cos / \sin(x - \pi/4)$. With this approximation, (5.9) becomes

$$M_{osc} \propto \sin(2\pi E_F/\hbar\omega_c) \cos(4\pi t/\hbar\omega_c - \pi/4) R_T.$$ \hspace{1cm} (5.13)

Considering that $\tau \propto 1/g(E_F)$ in equation (5.10) and substituting (5.12) and (5.8) into (5.10), the oscillatory resistivity $\sigma_{osc}$ becomes

$$\sigma_{osc} \propto \cos(2\pi E_F/\hbar\omega_c) \cos(4\pi t/\hbar\omega_c - \pi/4 + \Delta \phi) R_T$$ \hspace{1cm} (5.14)

where

$$\Delta \phi = \arctan(\hbar\omega_c/2\pi t)$$ \hspace{1cm} (5.15)

and again the trigonometric approximation for the Bessel functions has been used and higher harmonics have been omitted.

This model thus predicts the beating nodes of the dHvA and SdH oscillations to be shifted by $\Delta \phi$ on a 1/$B$-scale.
5.7.3 Discussion

Comparing the experimental observations to the model by Grigoriev et al. [33] described in the previous section, the following statements can be made right away:

- A phase shift between the SdH and the dHvA beating nodes as predicted by the model is indeed observed.

- The model predicts an increase of the shift with increasing magnetic field. Although this could not be seen at all tilting angles, it is the case for most of the observed angles. All these observed shifts at different fields overlap however within error bars.

The model does however not predict explicitly an angular dependence. In order to compare the experimental observations with the theoretical predictions, possible angular dependencies of the parameters determining the phase shift in the model should be considered.

Equation (5.15) relates the observed phase shift $\Delta \phi$ to the interlayer transfer integral $t$ only. Qualitatively looking at equation (5.15) shows that for $t \to 0$, $\Delta \phi$ should become large, which is indeed observed. Coming close to the beating zero at about $32^\circ$ means that the beating frequency $\Delta F$ tends towards zero. In the widely used model of a cosine modulated cylinder as the Fermi surface of a quasi-two dimensional metal (c.f. equation (4.1)), $\Delta F$ is related to $t$ in the following way: $4t/E_F = \Delta F/F$ where $E_F$ is the Fermi surface energy. This means that $t$ also tends towards zero, producing indeed a strong increase of the phase shift according to equation (5.15).

However, the arctan-function in equation (5.15) limits the maximum shift that can occur to $\pi/2$. Since this value is clearly surpassed in the experiment, the model presented here does not seem to be comprehensive in the sense of including all the important effects, but predicts qualitatively the behaviour that can indeed be observed. It can thus be concluded that the basic idea of the said model - i.e. the variation of the electron velocity with the magnetic field to be considered in the description of the transport process, plays probably an important role in producing the observed phase shift.

The remaining differences between theory and experiment may be due to two reasons:

- The approximations within the model are not sufficient for the range close to the beating zero.

- Other, not yet identified effects contribute to the observed phase shifts in a non-negligible manner.

Looking for a way to improve the theoretical description, it should be attempted to overcome the main restrictions of the model which are determined by its basic assumptions:

- semiclassical approach

- no explicit angular dependence

- no consideration of three-dimensional effects due to the relatively important warping of the Fermi surface.
5.7. COMPARISON WITH THEORETICAL MODELS

<table>
<thead>
<tr>
<th>Angle / deg.</th>
<th>Shift (lower dHvA node) / π</th>
<th>Shift (higher dHvA node) / π</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.8</td>
<td>0.71</td>
<td>-0.29</td>
</tr>
<tr>
<td>19.2</td>
<td>0.79</td>
<td>-0.19</td>
</tr>
<tr>
<td>20.7</td>
<td>0.76</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

Table 5.2: Shifts of the SdH node positions at high fields with respect to both the next dHvA node at lower field and the one at higher field. The experimental error for the positive shifts is about 0.07π, for the negative ones about 0.04π.

The question about the apparent jump in the shift as function of the temperature around 27 ° however persists. The interpretation of the increase of the shift being due \( t \) tending towards zero does not yield anything like this. As it has already been said, especially in this region, the determination of the phase shift is not very reliable. The phase shift given is based on an extrapolation that gets its input values from the positions of nodes in the low field range whose positions are difficult to determine. This could mean that the apparent jump would simply be due to the inaccuracy of the analysis in this region. It is however interesting to note that the jump seems to appear for shift values around \( \pi/2 \), where the tan-function as the inverse of the arctan-function in equation (5.15) has a singularity. In the experiment, however, the jump appears around shifts slightly higher than \( \pi/2 \), but especially in this angular region, extrapolation methods had to be used to calculate the phase shift, which might introduce an additional error.

However, it was tried to extrapolate the node positions assuming that Yamaji’s law holds and that phase shift as function of the tilting angle be continual. As it can be seen from figure 5.5, the node positions read from the raw data in this region are in the range 0.125 T\(^{-1}\), whereas an extrapolated value is rather in the region of 0.135 T\(^{-1}\). Although the raw data was thoroughly checked, no indications of a node at that field could be found either. Thus, the question about the true existence or not of the apparent jump cannot be finally answered at this point.

One might also speculate on the following:

As it was noted before, the existence of the jump - if confirmed - may be connected to the existence of the singularity of the tan-function at \( \pi/2 \). This hypothesis can be backed up as follows by looking at the high field data: at high fields (around 18T), the apparent phase shifts are scattered around \( 3\pi/4 \). This value exceeds obviously the limiting \( \pi/2 \) value. If, however, the shift is not measured between an SdH node and the adjacent dHvA node at lower field but instead to the one at higher field, negative shifts are obtained. In the case of the data presented in table 5.1, one gets those listed in table 5.2. Because at higher fields the signal-to-noise ratio is better, the corresponding dHvA node can be read with higher accuracy. This leads to a smaller error for the negative values listed in table 5.2 of about 0.04π.

Since the phase shift values listed in table 5.2 are measured within the same period, only with respect to different limits of the same, their difference is always \( \pi \), small deviations from that are within the experimental error as stated.

Because of the periodic properties of the tan-function

\[
\tan(x) = \tan(x + n\pi)
\]  

(5.16)
with \( n \) an integer, both values given for each angle in table 5.2 yield the same arctan-value. If this is the case, equation 5.15 can account for apparent phase shifts \( \pi/2 \) if a change of the sign of the shift. This would obviously result in a discontinuity of the phase shift.

In other words: what appears as a shift \( > \pi/2 \) might also be a negative shift. Along with the necessary change of the sign of the shift, a discontinuity of the shift can be expected.

Assuming that the condition for the occurrence of this discontinuity depends somehow on the argument of the arctan-function in equation (5.15), it is also plausible to assume that it can be inflicted by both, the magnetic field via the cyclotron frequency \( \omega_c \) and the tilting angle via the transfer integral \( t \). Such a change of the sign of the shift inflicted by the tilting angle might account for the apparent jump of shift 1 as function of the tilting angle (see figure 5.6). In principle, the same argument about the negative shift and the periodicity of the tan-function apply there as well, however, they cannot be checked rigorously against the experimental data there because only one dHvA node could be observed there and it is not a priori clear if the used extrapolation is valid.

The task of future work on the subject in order to check this idea would then be the following:

- **Experimentally:**
  - Verify the existence of the apparent jump or change of sign of the shift, both as function of the magnetic field and the tilting angle.
  - If the jump proves to exist, provide sufficient data to have at least both adjacent dHvA nodes for one observed SdH node.

- **Theoretically:** Check if a condition for a change of sign as described can be established.

### 5.8 Summary, Conclusions and Outlook

The results of simultaneous measurements of de Haas-van Alphen and Shubnikov-de Haas magneto quantum oscillations of \( \beta-(ET)_2\text{IBr}_2 \) have been presented and analysed. This system is quasi-two dimensional and exhibits pronounced warping of the Fermi surface. The resulting beating in the quantum oscillations is phase-shift when comparing the positions of the beatings in the de Haas-van Alphen and the Shubnikov-de Haas oscillations respectively. This experimental finding cannot be explained within the framework of the Lifshitz-Kosevich and the de Haas-van Alphen theories.

A theory developed by P. Grigoriev tries to explain the observed shift by assuming an oscillatory electron velocity as function of the magnetic field. The oscillation of the electron velocity is a consequence of the 2D-dispersion law. This effect competes with Shubnikov-de Haas oscillations as described by the Adams-Holstein theory. The superposition of these two oscillations leads to the observed phase shift. Since the de Haas-van Alphen effect is a completely thermodynamical equilibrium effect, the velocity oscillations do not affect it. The velocity oscillations change the beat phase of the Shubnikov-de Haas effect only, this latter effect being a disequilibrium effect including transport properties. The model
is semi-classical since it uses the quantisation in Landau levels, but the transport involved is described using the classical Boltzmann-equation.

The experimental findings are in qualitative accordance with the said model. A slight increase of the phase shift with increasing magnetic field can be observed for most angles. Where it cannot be seen, the deviations from such an assumption are still within error bars. The observed strongly increasing phase shift in close vicinity to the beating zero can be understood in terms of a smaller transfer integral, equivalent to a smaller and smaller beating frequency there. The prediction of the model, however, limits the phase shift to a maximum value of $\pi/2$ which can be seen surpassed spectacularly in the experiment.

This difference between the model and the experimental observation may have two reasons, which do not mutually exclude:

- The semi-classical nature of the model is not sufficient to describe the regime close to the beating zero.
- Other, not yet identified effects also contribute to the phase shift.

An apparent jump of the phase shift as function of the tilting angle around $27^\circ$ could not be confirmed definitely, neither excluded. Its verification must be left to further studies which should aim at having at least two observable de Haas-van Alphen nodes in the said angular regime. An experiment at a larger field range is necessary for that purpose. It might also be possible to explain the jump with a change of the sign of the shift.

Moreover, the question of a possible temperature dependence of the nodes has not yet been systematically studied either.
BEATING AND PHASE IN $\beta - (BEDT - TTF)_2IBr_2$
Chapter 6

Damping Effects in \( \kappa-(\text{BEDT-TTF})\text{Cu(NCS)}_2 \)

6.1 Introduction

The damping of the de Haas-van Alphen oscillation amplitude as function of several parameters is commonly used to extract system parameters such as the Dingle temperature and the effective electron mass. However, these methods of analysis depend on the applicability of the Lifshitz-Kosevich theory. This chapter is about a compound for which this validity cannot be assumed, shows and discusses the different amplitude behaviour, with a special emphasis on the effective electron mass analysis.

6.2 Presentation of the System

The quasi-two dimensional organic superconductor \( \kappa-(\text{ET})_2\text{Cu(NCS)}_2 \) is one of the most widely studied systems in this field of research. The system becomes superconducting at a critical temperature of about 10K and ambient pressure. This critical temperature is relatively high compared to other organic superconductors, but is however a common feature of all the \( \kappa \)-phase systems, although some of them demand for moderate pressures to exhibit superconductivity.

Crystallography

The crystal structure is shown in figure 4.2. Room temperature crystallographic data are: \( a=16.256\text{Å}, b=8.456\text{Å}, c=13.143\text{Å}, \alpha = 90^\circ, \beta = 110.28^\circ \) and \( \gamma = 90^\circ \) [97].

Electronic Properties

Energy dispersion relation and Fermi surface of this compound have been modeled using the extended Hückel tight binding method [70][111][71] [98] and confirmed by dHvA and SdH experiments. The calculated two-dimensional bandstructure and Fermi surface is shown in figure 6.1.
Figure 6.1: Calculated bandstructure and Fermi surface of $\kappa$-(ET)$_2$Cu(NCS)$_2$ [70][111][71] [98].

The first quantum oscillations in this system were reported in 1988 [70] and for quite a long time this had been the only system of the $\kappa$-family in which quantum oscillations could be observed.

In principle, all the $\kappa$-compounds are expected to have similar Fermi surfaces and thus to yield similar results in magneto quantum oscillation experiments. However, $\kappa$-(ET)$_2$Cu(NCS)$_2$ does not follow the usual scheme as it exhibits an unusual field and temperature dependence of the effective mass. Firstly, it was tried to explain this as result of a quasi-two dimensional warping of the Fermi surface [118][51] [75], however, AMRO experiments did not reveal any warping of the Fermi surface and thus call for another explanation of this phenomenon [51]. One possible explanation could be the existence of additional, quasi-one dimensional parts of the Fermi surface [54]. This could also help explaining the unusual angular dependence of the magnetic breakdown orbit dHvA-amplitude observed for this compound [115]. Indeed, the bandstructure model presented in figure 6.1 shows two open sheets.

The typical quantum oscillation spectrum of $\kappa$-(ET)$_2$Cu(NCS)$_2$ exhibits two fundamental frequencies labeled $\alpha$ and $\beta$. The corresponding orbits can be seen in figure 6.1. The so-called $\alpha$-orbit corresponds to the closed parts of the Fermi surface that can be seen on the borders of the Brillouin zone, the orbit of the so-called $\beta$-orbit is made up by the outer parts of the closed parts, completed by the open sheets. At the gap between the two of them, the electrons must tunnel from the open to the close part and vice-versa. The probability of this tunneling process increases with increasing magnetic field, an effect known as magnetic breakdown.

The $\beta$-orbit can occur under conditions of magnetic breakdown only and consequently appears at high fields only. In addition to these fundamental frequencies, harmonic oscillations, sum and difference frequencies of these two fundamental oscillations can be observed. It is worth noting that in this compound also the so-called "forbidden orbits", i.e. $F_{\beta-a}$, $F_{\beta-2a}$ and $F_{2\beta-2a}$ have been observed. In the semi-classical coupled-network model [73] that is usually used to explain the occurrence of difference frequencies would require an inversion of the direction of motion at least once to create the necessary orbit. An extensive discussion of the experimental findings on this phenomenon as well as a comparison with the predictions of various theoretical models can be found in [37].

Far-infrared reflectance experiments [43] yielded a cyclotron mass of $m_c \approx 1.2m_e$, that is considerably lower than the effective electron mass from dHvA experiments. This has
been interpreted as an indication of strong electron-electron interaction within the low-dimensional Fermi liquid. Even the occurrence of a Luttinger liquid in this compound has been proposed on grounds of the absence of a sharp Fermi edge and corresponding low density of states at the Fermi energy [66].

Moreover, this compound is one of the few where it has been possible to observe dHvA oscillations in the superconducting vortex state [103][102].

6.3 Motivation

The main motivation for the high field experiments described in this chapter was a suspected deviation from the $1/\cos \theta$ dependence of the effective mass as reported in [116]. The suspicion was grounded on previous measurements carried out by Meyer, Nguyen and Steep [37] [93].

6.4 Choice and Characterisation of the Sample

Previous results giving rise to the suspicion of the existence of anomalies in the effective electron mass as function of the tilting angle towards the magnetic field indicated that a low Dingle temperature might be favourable for the occurrence of the effect. Thus, measurements of the dHvA effect were performed on various crystals in the superconducting magnet in order to choose one exhibiting no serious crystallographic defects such as twinning and having a Dingle temperature as low as possible.

6.4.1 Dingle Plot

Making use of the field dependence of the de Haas-van Alphen amplitude as described by the terms $R_D$ and $R_T$ in the Lifshitz-Kosevich formula (1.11, 1.18, 1.16), the Dingle temperature $T_D$ and hence a measure for the amount of scattering centres in the sample can be extracted. This procedure starts with the amplitude $A$ given in arbitrary units as $A = R_T R_D$. Putting (1.18) and (1.16) into this expression and equivalence transformations yield:

$$- \frac{\alpha m^* / m_e T_D}{B} = \ln \left[ \frac{A \sinh (\alpha m^* / m_e T / B)}{\sqrt{B} \alpha m^* / m_e T / B} \right]$$  \hspace{1cm} (6.1)

Thus, plotting the right-hand side of equation (6.1) as function of $1/B$ will yield a straight line with the slope $-\alpha m^* / m_e T_D$, so that with the effective electron mass $m^*$ and the temperature $T$ known, the Dingle temperature $T_D$ can be extracted. Equation (6.1) is valid for the torque amplitude $A$, that means that the amplitude is divided by a factor $B$ in order to compensate for the factor $B$ in equation (3.1).

The Dingle plot for the sample finally chosen is shown in figure 6.3. With $T = 463mK$ and $m^* = 3.7m_e$, a Dingle temperature $T_D = 447mK$ is found.
Figure 6.2: Characterisation dHvA measurement: oscillations of the magnetisation at $T=463\, \text{mK}$. The tilting angle of the sample with respect to the magnetic field is $24.5^\circ$. Non-oscillating contributions to the magnetisation have been subtracted.
Figure 6.3: Dingle plot generated from the set of data shown in figure 6.2. $D(B)$ is defined by equation (6.1).

$T_D = 447 \text{mK}$

$m_{\text{eff}} = 3.7m_e$
6.5 Angular Dependence of the Apparent Effective Electron Mass

6.5.1 Evaluation Procedure

The effective electron mass was determined from the temperature dependence of the dHvA amplitude using the temperature dependent prefactor of the Lifshitz-Kosevich formula (1.11) as expressed in equation (1.16). The dHvA oscillations were recorded at five different temperatures (0.4K, 0.6K, 0.8K, 1.0K, 1.4K) in the field range from 19T to 22.6T. For each temperature, a fast Fourier transform was performed to determine the amplitude. The expression (1.16) was then fitted to the data, taking the temperature \( T \) as the independent variable and the magnetic field \( B \) approximated by the constant mean value \( \bar{B} = 20.75T \) was used. The effective mass \( m^*/m_e \) was then varied in order to give the best fit to the experimental data using the Levenberg-Marquardt fitting algorithm.

Figure 6.4 shows such a set of data and figure 6.5 shows the amplitude as function of temperature obtained from this set of data together with an example of fitting the data to expression (1.16).
Figure 6.5: De Haas-van Alphen oscillation amplitudes obtained from the set of data shown in figure 6.4 as function of temperature. The temperature factor (1.16) is fitted to these points in order to determine the effective electron mass.
6.5.2 Angular Dependence of the Effective Electron Mass

General Description

Measurements of the de Haas-van Alphen oscillation amplitude as function of the temperature were carried out at different tilting angles and for two different orientations of the rotational axis. The two different axes with respect to the crystal morphology are shown in figure 6.6. They will be referred to hereafter as orientation "1" and "2" in the way indicated in figure 6.6.

In the experimental results, the $\alpha$-frequency $F_\alpha$ was present at all orientations. In many orientations, the harmonic frequency $F_{2\alpha}$ could also be observed. Occasionally, the $\beta$-frequency $F_\beta$ was also present and sometimes their mixing products $F_{\beta-\alpha}$, $F_{\beta+\alpha}$ etc. as well. The latter, in general, however were of small amplitude and could only be seen in some measurements carried out at the lowest temperatures available in this series. Sufficient data for an effective mass analysis were obtained for the frequencies $F_\alpha$ and $F_{2\alpha}$. The results obtained are shown in figure 6.7. All masses shown in this figure have been observed in orientation 2. The masses given for the harmonic frequency are obtained with a harmonic factor $p = 2$ inserted into the term (1.16). Other authors use the convention to keep this factor equal to one, regardless of the fact which harmonic is analysed. If results that are given within the framework of the latter convention are to be compared to the results presented in this work, the masses given in this work have to be multiplied with a factor of two to be consistent with the results to be compared with.

![Figure 6.6: The two different orientations of the rotational axis at which measurements of the effective electron mass were carried out.](image-url)
The error bars correspond to 95% confidence intervals as resulting from the Levenberg-Marquardt fitting algorithm.

The figure shows also two fits that have been obtained by fitting a $m_0/\cos(\theta)$-model to the data points on the side of angles with a negative sign. Best fits are obtained for the following values of the zero angle mass $m_0$:

\begin{align*}
  m_0^\alpha &= (3.25 \pm 0.2)m_e \quad \text{(6.2)} \\
  m_0^{2\alpha} &= 2.6m_e. \quad \text{(6.3)}
\end{align*}

Again, the error represents a 95% confidence interval for the fit parameters. For the $2\alpha$ data, no confidence interval could be calculated because only two points of data went into the fit.

The fit was done without leaving a free parameter to account for a possible shift of the zero of the angular scale. This was done because the angles have been determined directly from the observed de Haas-van Alphen frequency.

The measurements concentrate on angles around 35° because previous results indicated an irregular behaviour there whereas the behaviour other angular ranges was found to be regular.

In addition, two masses were determined in orientation 1. At the position 38.4°, $m_0^\alpha = (4.17 \pm 0.03)m_e$ was found and at -41.2°, a mass of $m_0^{2\alpha} = (3.8 \pm 0.05)m_e$ could be observed.

The results obtained in orientation 2 are summarised in figure 6.7.

As can be seen in figure 6.7, the experimental results in the negative angle range follow the expected $1/\cos(\theta)$ behaviour, whereas this is not the case for the regime of positive angles. There is no symmetry around the zero position.

Moreover, the results for the harmonic frequency $F_{2\alpha}$ do not yield the same effective mass as the analysis of the data obtained from the $F_{\alpha}$ data.

In addition, in orientation 1, the following two masses could be determined:

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$m_0^\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.4°</td>
<td>4.17$m_e$</td>
</tr>
<tr>
<td>-41.2°</td>
<td>3.9$m_e$</td>
</tr>
</tbody>
</table>

The excessive error at the angle 30.3° is due to an anomalous dependence of the de Haas-van Alphen amplitude on the temperature which makes it difficult to evaluate for an effective electron mass as this position. Figure 6.8 shows this behaviour together with the fit curves. If the point at 0.4K is ignored in the fitting process, effective electron masses of $m^\alpha = (7.7 \pm 0.1)m_e$ and $m^{2\alpha} = (4.2 \pm 1.5)$ are obtained. A further measurement was carried out at an angle of 26.1°. The data of this measurement did not allow for any effective electron mass analysis at all. The temperature dependence found at this position is shown in figure 6.9.

The measurements mainly concentrate on angles $|\theta| > 30^\circ$ because the $1/\cos(\theta)$ dependence of the effective electron mass is not questioned by the previous results having stimulated these experiments. A comparison with these results will be given in the discussion.

Some irregular behaviour of the effective electron mass on the side of positive angles is clearly visible.
Figure 6.7: Effective electron masses observed in $\kappa$-(ET)$_2$Cu(NCS)$_2$ as function of the tilting angle in orientation 2 extracted from the observed oscillations at the fundamental frequency $F_\alpha$ and the harmonic frequency $F_{2\alpha}$. The lines show fits to the data obtained from the points on the side of negative angles to a $1/\cos(\theta)$ behaviour. The solid line represents a fit to the fundamental frequency mass $m_\alpha$ and the dashed one corresponds to the harmonic frequency mass $m_{2\alpha}$.
6.5. **Angular Dependence of the Apparent Effective Electron Mass**

Figure 6.8: Temperature dependence of the de Haas-van Alphen amplitude at 30.3°.

Figure 6.9: Temperature dependence of the de Haas-van Alphen amplitude at 26.1°.
The comparison of the points to the fit shows clearly the non $1/cos(\theta)$ behaviour of the effective electron mass for angles $\theta > 25^\circ$. There is, however, no corresponding deviation from the $1/cos \theta$ behaviour on the side of negative angles.

In orientation 1, an effective mass of $4.17m_e$ was measured at an angle of $38.4^\circ$ and one of $3.8m_e$ at $-41.2^\circ$.

6.6 Discussion

The observation of the apparent effective electron mass of $\kappa$-(ET)$_2$Cu(NCS)$_2$ as function of the tilting angle $\theta$ with respect to the magnetic field yielded several deviations from the behaviour that can be expected from a simple quasi-two dimensional system: the observed dependence does not follow a $1/\cos(\theta)$ law. Moreover, there is no symmetry around the zero position. The discussion of these experimental observations will be organised as follows: first, the findings will be discussed in the framework of known properties of the system. This includes a comparison with experimental findings made by other researchers in the field. After that, possible artefacts that could lead to these observations will be discussed and ruled out as far as possible. Then, an attempt is made to compare the findings with the predictions of theoretical models that consider the specific conditions of a two-dimensional electron system.

6.6.1 Range where Deviations from Lifshitz-Kosevich Behaviour Occur

In orientation 2, the most dramatic deviations from $1/\cos(\theta)$ behaviour were observed at a tilting angle of about $30^\circ$. Here, not only the absolute values of the determined effective electron masses differ significantly from the values that could be expected assuming a $1/\cos(\theta)$ model, also the temperature dependence differs significantly from the behaviour that could be expected from the Lifshitz-Kosevich formula. This latter circumstance is indicated by the excessive range of the error bars ($\approx$ confidence intervals of the fit parameters) in that range, notably at the measurement carried out at $30.3^\circ$. An extreme case could be observed at an angle of $26.1^\circ$, where the temperature dependence of the de Haas-van Alphen amplitude deviates so strongly from the prediction of the Lifshitz-Kosevich theory that practically no meaningful analysis for an effective electron mass was possible at that angle.

Looking more closely at the range from roughly $20^\circ$ to $40^\circ$, it appears that around the limits of the investigated angular range, the effective electron mass determined from the frequency $F_\alpha$ ($F_\alpha$-mass) tends to a ”normal”behaviour in the sense that it approaches once again the $1/\cos(\theta)$ behaviour.

The behaviour of the $F_{2\alpha}$-mass is extraordinary in various aspects. First, it is generally not the same as the $F_\alpha$ mass which normally would be the expectation when the temperature factor (1.16) of the Lifshitz-Kosevich formula (1.11) is used as a fit function in the convention that the harmonic is considered by an appropriate choice of the index $p$.

About the angular dependence, it can be observed that on the ”regular”-side, that is the range of negative angles where the $F_\alpha$-mass exhibits a regular $1/\cos \theta$ dependence, the $F_{2\alpha}$-mass also follows this regularity, although it with another zero angle mass.

On the side of positive angles, where irregularities are observed for the $F_\alpha$-mass, the $F_{2\alpha}$-mass also deviates significantly from a $1/\cos \theta$ dependence. It does however not
follow qualitatively the behaviour of the $F_\alpha$-mass. While the former appears to be almost regularly angle dependent at lower angles and then run into irregular behaviour, the tendency of the $F_{2\alpha}$-mass seems rather to be to approach the regular behaviour - that is the $1/\cos\theta$-extrapolation based on the fit of that model to the observations on the side of negative angles - coming from lower values, with some sort of maybe a peak around $30^\circ$.

Looking at orientation 1, the two observed masses are now compared to the $1/\cos\theta$ model using the zero angle mass determined by the "regular" points in orientation 2. This mass was $(3.3 \pm 0.2)m_e$. Taking that as the base, the following expected values can be determined and are compared to the observed ones:

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$m_\alpha^{\text{expect}}/m_e$</th>
<th>$m_\alpha^{\text{observe}}/m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$38.4^\circ$</td>
<td>$4.21 \pm 0.26$</td>
<td>$4.17 \pm 0.03$</td>
</tr>
<tr>
<td>$-41.2^\circ$</td>
<td>$4.38 \pm 0.27$</td>
<td>$3.8 \pm 0.05$</td>
</tr>
</tbody>
</table>

Thus, also in this orientation a deviation of the effective electron mass from the $1/\cos\theta$ expectation can be observed and again it can be observed for just one side only, there is also an asymmetry as it was observed in orientation 2.

### 6.6.2 Comparison with Results Obtained by Others

The experimental study of the effective electron mass of $\kappa$-(ET)$_2$Cu(NCS)$_2$ has been motivated mainly by previous results obtained by Meyer, Nguyen and Steep [37][93]. The results presented in the previous section will now be compared with the results of these authors. The results obtained by Wosnitza and co-workers [116] are also considered as these represent the first systematic study of the effective electron mass of the compound in question.

**The $F_\alpha$-mass**

The results of this work are compared to the results obtained by Nguyen [37] and those of Wosnitza and co-workers [116].

Figure 6.10 shows the results of this work in comparison with Nguyen’s.

Both sets of data show considerable deviations from the $1/\cos\theta$ behaviour in the angle range of about $20^\circ$ to $45^\circ$. In the range $\leq 20^\circ$, Nguyen’s results seem to be consistent with a $1/\cos\theta$ model, although with a slightly smaller zero angle mass than in the data obtained within this work. Also in the range of deviations from the $1/\cos\theta$-expectation, Nguyen’s masses are slightly below the ones obtained within the framework of this work. If an overall shift of about $0.15m_e$ is assumed, the two sets of data would show roughly the same effective mass values. This latter observation seems to hold for the whole depicted angular range, in the regular and the irregular parts.

There seems to be a minimum around $26^\circ$ to $27^\circ$, although no data is available for this range. This corresponds to the angle where a maximum deviation of the de Haas-van Alphen amplitude as function of temperature from the Lifshitz-Kosevich theory was observed in this work. Nguyen also observed the deviation from Lifshitz-Kosevich behaviour at this angular range as she states in [37].

A remarkable qualitative feature that is visible in the data obtained within the framework of this work and that does not appear in Nguyen’s data is the relatively high mass
Figure 6.10: Effective electron mass analysis for the $F_\alpha$ mass by Nguyen compared to the results of this work. A plot of $3.25/\cos \theta$ is also shown. Nguyen’s results are from [37].

at 30.3°. One could suspect some sort of sharp maximum there, but on the other hand, the error becomes excessive there as a result of the non-Lifshitz-Kosevich temperature dependence of the de Haas-van Alphen amplitude there so that this cannot be said with certainty.

Summing up, it can be said that the occurrence of non-Lifshitz-Kosevich dependencies of the de Haas-van Alphen amplitude on angle and temperature for the range from 20° to 45° appears in both measurements. The exact manifestation of the irregularity is not the same for the $F_\alpha$-mass, but not contradictory either if one accounts for the experimental errors.

Finally, the results of Wosnitza et al. [116] are to be considered. They are shown in figure 6.11 and apply for the $F_\alpha$-frequency. Although the authors concluded at the time that the mass follows a $1/\cos \theta$ dependence for the whole examined range, it is worth noting that on their side of negative angles the experimental data is scattered further off the fit function than it is the case on the side of positive angles. This was not considered as significant at the time, but may be of interest in the present context, where an asymmetric deviation is discussed. Wosnitza et al. do not show any data for the range of about 26° to 27°. It seems however worth noting that also in their data there is one point considerably above the others, that is the one at about -40°. It is, however, about 10° off the angle at which the peak value was observed in this work. Wosnitza et al. obtained a zero angle mass of $(3.24 \pm 0.2)m_e$ for the best $1/\cos \theta$ fit which is consistent with the result of $(3.25 \pm 0.2)m_e$ obtained in this work. Although some irregularities can also be seen in
6.6. DISCUSSION

Figure 6.11: The $F_\alpha$ mass as function of the angle as obtained by Wosnitza et al. From [116].

the results of Wosnitza et al. and although these were not regarded as significant by the authors at the time, this is not necessarily a contradiction to the findings of Nguyen and the ones presented in this work.

The $F_{2\alpha}$-mass

Nguyen’s results for the $F_{2\alpha}$-mass are presented in figure 6.12 together with the results of this work to be compared.

Comparing the masses obtained in this work to Nguyen’s results as shown in figure 6.12, an agreement within the experimental error can be stated. Around $35^\circ$, both graphs show masses that are scattered around about $3m_e$ (in $p = 2$ convention). At about $20^\circ$, Nguyen obtains a mass of $2m_e$ which overlaps with the value of $2.2m_e$ found in this work within error bars. Nguyen’s data seem to indicate a minimum around $26^\circ$, although she was not able to perform an effective electron mass analysis for the $2\alpha$ orbit at this position. It seems however worth noting that this suspected minimum corresponds to the position where the strongest deviations of the de Haas-van Alphen amplitude as function of the temperature were observed in this work. The qualitative behaviour of the effective electron mass coming up from lower values at angles around $35^\circ$ can also be seen in Nguyen’s results.

Asymmetry

Nguyen [37] also reports an asymmetry for the two directions of tilting around a specific rotational axis. However, she reports it only for the rotation around the $b$-axis, that is orientation 1 in the convention of this work. She explains with the asymmetrical bending
Figure 6.12: Effective electron mass analysis for the $F_{2\alpha}$ mass by Nguyen compared to the results of this work. Nguyen’s results have been divided by 2 in order to be comparable to the results of this work considering the different conventions used. Nguyen’s results are from [37].


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of the anion molecule within the crystal structure.

Summary of the Comparison with Other Results

Nguyen [37] finds deviations from the $1/\cos \theta$ behaviour for both the $F_\alpha$ and the $F_{2\alpha}$ mass in the same angular ranges. Whereas for the $F_{2\alpha}$-mass, the agreement between the two sets of data is quite well within the experimental error, the qualitative shape of the irregularity is difficult to determine, mainly due to the irregular dependency of the de Haas-van Alphen amplitude on the temperature in the angular range concerned. However, the irregularities could be confirmed in their existence for the same angular range and they do not contradict each other within the experimental error, which is - however - large, again as a result of the irregular temperature dependence already mentioned. The results of Wosnitza et al. [116] do also show some asymmetry around the zero position, but the effect is less pronounced so that it was not regarded as significant by the authors at the time. The observed asymmetry is in accordance with statements by Nguyen on the subject and possibly due to the asymmetrical bending of the anion molecule [37].

6.6.3 Usefulness of the Lifshitz-Kosevich Theory for $\kappa-(ET)_2Cu(NCS)_2$, Deviations, Meaning of the Apparent Effective Electron Mass

Summing up the discussion that has taken place up to here, the following can now be said about the experimental situation:

- Irregular behaviour of the effective electron mass as function of the angle occurs at angles $\geq 20^\circ$ on two perpendicular rotational axes. These axes were chosen along symmetry axes of the crystal. ”Irregular” means that they do not follow a $1/\cos \theta$ dependence.

- In the same angular region, the $F_{2\alpha}$-mass is also irregular in the sense that it does not correspond to the $F_\alpha$-mass as expected by Lifshitz-Kosevich theory.

- Non-Lifshitz-Kosevich temperature dependence occurs in this angular region, most pronounced for angles about $25^\circ$ to $30^\circ$.

- These irregularities have been observed independently in at least two different experiments on two different samples. A third experiment on a third sample shows less pronounced effects, but is not necessarily contradictory.

These observations, together with the statement given in the presentation of the system at the beginning of this chapter that the effective electron mass values obtained by quantum oscillation experiments differ significantly from the cyclotron masses observed in far-infrared reflectance experiments, give rise to the question if Lifshitz-Kosevich theory is applicable to this system at all.

The Lifshitz-Kosevich theory is a theory describing a three-dimensional system whereas this system here is basically a two-dimensional one. Generally, the Lifshitz-Kosevich theory can be used to describe a quasi-two-dimensional system, i.e. a two-dimensional system with residual electron interaction between the conducting sheets exists. Such a residual interaction would result in a corrugation of the Fermi surface and thus in the occurrence
DAMPING EFFECTS IN $\kappa$-(BEDT-TTF)Cu(NCS)$_2$

of two slightly different quantum oscillation frequencies that would cause nodes in the observed quantum oscillations. Such nodes, however, could not yet be observed in this system.

On the other hand, for a truly two-dimensional system, saw-tooth shaped quantum oscillations are to be expected [90]. These have not yet been observed either, as can be seen for example in figure 6.4, the waveform is almost perfectly sinusodial. Some deviations occur due to the occurrence of the $2\alpha$ and the $\beta$ frequencies, but the waveform is however far from saw-tooth. It is however possible for a two-dimensional electron system to exhibit sinusodial oscillations when an electron reservoir is present in the form of an open Fermi surface sheet. In $\kappa$-(ET)$_2$Cu(NCS)$_2$, such a reservoir could be provided by the open Fermi surface sheet that by tunneling in the magnetic breakdown regime gives rise to the $\beta$-frequency together with a part of the $\alpha$-orbit. The question about the true dimensionality of $\kappa$-(ET)$_2$Cu(NCS)$_2$ - truly two-dimensional or quasi-two dimensional - is not finally answered at this time.

However, the experimental evidence shows that significant deviations from the Lifshitz-Kosevich theory are exhibited by this system. A theory describing the observed effects should therefore be able to yield an expression for the oscillatory magnetisation analogous to equation (1.11) that describe correctly the observed amplitudes dependencies, starting from the specific conditions present in this system.

As there are severe doubts about the applicability of Lifshitz-Kosevich theory to this system and the effective mass analysis within its framework is based on the amplitude dependencies of the quantum oscillations, it seems to be appropriate at this point of the discussion not to speak about the behaviour of the effective electron mass anymore, but rather about the dependence of the quantum oscillation amplitude on angle and temperature. This latter point is supported by the observation that infra-red reflectance yields a very different cyclotron mass than the effective electron mass found by quantum oscillation experiments analysed within the Lifshitz-Kosevich context.

6.6.4 Theoretical Models

The most important difference between the theoretical treatment of two dimensional and three dimensional electron systems is that in the first case under the constraint of a fixed number of particles the chemical potential becomes an oscillatory function of the inverse magnetic field. Any theory of the de Haas-van Alphen effect is concerned by this.

Yamaji [118] gives the spectrum for a quasi two-dimensional electron system in a field tilted by an angle $\theta$ with respect to the Fermi surface cylinder axis as follows:

$$E(\theta) = \omega_c \cos \theta \left( n + \frac{1}{2} \right) - 2t J_0(k_F t \tan \theta) \cos(k_z d). \quad (6.4)$$

Here, $J_0$ is the Bessel function of zero order, $k_F$ is the momentum at the Fermi energy, $d$ the distance between adjacent conducting planes in real space, $t$ the transfer integral between adjacent conducting planes, $k_z$ the part of the momentum vector parallel to the magnetic field and $\omega_c$ is the cyclotron radius. Additional terms in (6.4) accounting for spin energy and band energy have been omitted here because they are independent of $\theta$.

Depending on the value of the transfer integral $t$, the Bessel term modifies the usual two dimensional spectrum by an angular dependent term. This modification is most
prominent around $\theta = 90^\circ$ where the tangent in the argument of the Bessel function diverges. However, the most prominent deviations from Lifshitz-Kosevich theory observed experimentally were found around $\theta \approx 25^\circ\ldots30^\circ$, where the modification by the Bessel term is rather moderate. This could indicate that the oscillation of the chemical potential alone may not account for the deviations from Lifshitz-Kosevich theory observed in the experiments described in this work. However, so far there is no analytical expression for the spectrum of quantum oscillation frequencies starting with the quasi-two dimensional energy spectrum (6.4). Champel and Mineev, who took up the matter in [17], use a simplified energy spectrum that is valid at zero tilting angle only.

On the other hand, the angular range in which deviations from Lifshitz-Kosevich behaviour have been observed in the course of the present work coincides with the range in which the magnetic breakdown frequency $F_\beta$ together with the sum and difference frequencies occurs. Therefore, theoretical models discussing magnetic breakdown under the conditions of oscillating chemical potential shall be regarded.

### 6.6.5 Numerical Calculations by Nakano

Nakano [69] performed numerical calculations of the amplitude of the dHvA oscillations of the various fundamental frequencies and their combinations as function of the tilting angle in a multiband system with chemical potential oscillations and considering the AMRO behaviour. He found the most prominent deviations of the amplitude behaviour at angles of about $30^\circ$. The bandstructure he assumed is made up to model the High-$T_c$-superconductor Sr$_2$RuO$_4$, and it is not clear how changes of particular parameters in his bandstructure affect the result of the numerical calculation. For this reason, it is very difficult to give a direct comparison with these results.

### 6.6.6 Model by Champel

Champel developed a model describing the de Haas-van Alphen effect in a two-dimensional multiband system considering chemical potential oscillations [16]. This model starts from a thermodynamic calculation of the magnetisation and then shows that via the oscillation of the chemical potential, the following deviations from Lifshitz-Kosevich behaviour may occur:

- the occurrence of the so-called forbidden combination frequencies
- amplitudes other than those predicted by Lifshitz-Kosevich for all frequencies occurring, including the fundamentals.

For the following approximative Fourier series representation of the magnetisation, the model assumes a two-dimensional system with chemical potential oscillations that are "small" in the sense that if - hypothetically - they would be switched off, the change of the amplitude of the magnetisation oscillation would differ only by a small amount compared to its total value.

The oscillatory magnetisation is then given as:
DAMPING EFFECTS IN $\kappa$-(BEDT-TTF)$\text{Cu(NCS)}_2$

$$M_{osc} = \sum_{\alpha,l} M_{0\alpha} A^l_{\alpha} \sin \left( 2\pi l \frac{F_{\alpha}}{\hbar \omega_{\text{ca}}} \right)$$

$$+ \sum_{\alpha,\alpha',l,l'} \frac{\pi l}{1 + R m_e} M_{0\alpha} A^l_{\alpha} A^l_{\alpha'} \sin \left( 2\pi l' \frac{F_{\alpha}}{\hbar \omega_{\text{ca}}} \right) \cos \left( 2\pi l \frac{F_{\alpha}}{\hbar \omega_{\text{ca}}} \right). \quad (6.5)$$

In equation (6.5), the $A^l_{\alpha}$ represent the non-oscillating amplitude factors, the indices $\alpha$ enumerate the bands, $l$ the harmonics, $R$ is a parameter measuring a possible electron reservoir damping the chemical potential oscillations, $F_{\alpha}$ is the quantum oscillation frequency of each band and $\hbar \omega_{\text{ca}}$ the cyclotron energies.

The second term in equation (6.5) contains terms producing the combination frequencies and others modifying the amplitudes of the fundamental frequencies and their harmonics. As in the experimental results were obtained for $F_{\alpha}$ and $2F_{\alpha}$, the main interest is focused on these latter ones.

According to [16], the ratio of the usual amplitude - the one that occurs without chemical potential oscillations - to the amplitude with chemical potential oscillations of the $L$th harmonic of a frequency $F$ is given by the terms $L = l \pm l'$ of (6.5), in case of the first harmonic - i.e. the fundamental - this ratio is given by

$$1 - \frac{\pi}{2(1 + R) m_e} \frac{1}{A^l_{\alpha}} \sum_{l=1}^{\infty} A^l_{\alpha} A^{l+1}_{\alpha}. \quad (6.6)$$

The exact behaviour of the second term in (6.6) now depends on the exact behaviour of the $A^l_{\alpha}$ and will thus strongly depend on parameters such as tilting angle, temperature etc.

However, it has now been demonstrated that deviations from the Lifshitz-Kosevich behaviour can be accounted for by oscillations of the chemical potential. The presence of the forbidden frequencies in the compound studied [37] indicates the presence of chemical potential oscillations in this system. It should however be noted that in 6.6, only the parameters for the fundamental itself and its harmonics enter: the existence of the modification described by (6.6) is thus independent of the existence of another frequency in the system. Experimentally, the deviations from Lifshitz-Kosevich behaviour seem to occur preferably in the magnetic-breakdown regime. If this is really correlated or pure coincidence cannot be decided on grounds of equation (6.6)

On the other hand, the modification term in (6.6) seems to indicate some of the qualitative behaviour observed: the amplitudes $A^l_{\alpha}$ are proportional to a factor $(-1)^{l+1}$, which means that the sum in (6.6) will be negative. Consequently, the correction will be positive, the amplitude will be increased, especially if $A^l_{\alpha}$ becomes small, a very strong increase might be expected.

The effective mass in Lifshitz-Kosevich formalism is determined experimentally by a fit of the temperature dependent amplitude to a term of the form $\beta m^* T / \sinh(\beta m^* T)$ (c.f. (1.16)). Thus, an increase of the observed amplitude under otherwise unchanged conditions may suggest a higher effective mass. Looking again at figure 6.7 seems to indicate some sort of peak of the $F_{\alpha}$-mass around 25...30°.
6.7 Artefact Exclusion

Naturally, the question arises if the observed modifications may be due to an experimental artefact such as torque interaction. This can - however be excluded for the following reasons:

- The oscillation amplitude is of comparable order of magnitude for both tilting senses if the angle is the same. Deviations, however, occur only on one side.

- The experimentally observed capacitance change was in the range of some per cent of the total capacitance only.

- Nguyen performed systematic comparison experiments between an uncompensated torque measurement as it was done in the frame of this work and compensated torque experiments. In the latter, a small coil on the leaf spring is used to create a field locally compensating the magnetisation of the sample. The magnetisation is measured by the current needed to reach compensation, i.e. to restore the leaf spring to its initial position. Thus, the sample is always kept in the same position with respect to the magnetic field and torque interaction cannot occur. She did not find any significant differences between compensated and uncompensated measurements under conditions similar to the ones of the experiments described in the present work.

For these reasons, torque interaction can be excluded as origin of the observed deviations.

6.8 Summary and Conclusions

Summarizing and concluding, the following statements can be made:

- Significant deviations of the de Haas-van Alphen oscillation amplitude have been observed in $\kappa$-(ET)$_2$Cu(NCS)$_2$.

- This behaviour occurs asymmetrically: tilting the sample by the same amount in two directions around the same axis yields regular Lifshitz-Kosevich behaviour on one side and irregular behaviour on the other. This can be understood in terms of the known asymmetric bending of the anion molecule in this compound.

- The experimental findings are in accordance with earlier results by Nguyen, Meyer and Steep [37] [93]. Earlier results by Wosnitza et al. [116] do not show clearly the deviations from Lifshitz-Kosevich behaviour, however, small deviations can also be seen in their data although this was not regarded as significant at the time. The
results of Wosnitza et al. were obtained at lower fields which might explain that the effect was less apparent in their experiment.

- An analysis of the effective electron mass in the Lifshitz-Kosevich context does not make sense in the angular regions significant deviations. The apparent effective mass is significantly modified.

- A theoretical model by Champel [16] yields arguments that show some qualitative accordance with the experimental findings. The main physical input to this model is the assumption of the existence of chemical potential oscillations in a two-dimensional system. The experimentally verified existence of the so-called "forbidden"orbits in $\kappa$-(ET)$_2$Cu(NCS)$_2$ [37] shows the occurrence of chemical potential oscillations in this system.

- Experimentally it seems that the most significant deviations from Lifshitz-Kosevich behaviour occur at angles where magnetic breakdown occurs. This, however, is not necessarily a condition to modify the amplitudes of non-combination frequencies within the context of Champel’s theory.

- It seems to be that the observed deviations from the Lifshitz-Kosevich prediction are due to the occurrence of chemical potential oscillations, i.e. connected with a significant two-dimensional character of the system. The asymmetry of this system produces the deviations however on one side only. This would offer the interesting possibility of studying the quasi three-dimensional and the quasi two-dimensional case on one and the same system by simply changing the angle.

- Significant torque interaction can be excluded.
Chapter 7

Investigations on the Electronic Structure of $\alpha_T$-(BEDT-TTF)$_2$I$_3$

7.1 Motivation

The compound $(\text{ET})_2$I$_3$ has been synthesised in a variety of crystallographic phases exhibiting electronic properties that differ significantly one from the other. The $\alpha$--phase as synthesised shows an insulating phase at low temperatures but a thermal treatment transforming it to the so-called $\alpha_T$--phase yields a completely different low temperature behaviour: the system now shows a superconducting transition at about 7K, together with a metallic behaviour above that temperature. The nature of this structural phase transition is unclear. An attempt was made to shed some light on this question by trying to extract some information about the electronic structure of the $\alpha_T$--phase by the possible occurrence of magneto quantum oscillations.

7.2 Presentation of the System

7.2.1 Preparation

The compound $\alpha_T$-(ET)$_2$I$_3$ is an organic superconductor that is obtained by subjecting specimens of $\alpha$-(ET)$_2$I$_3$ to a thermal treatment. Typically, single crystals of $\alpha$-(ET)$_2$I$_3$ are heated to temperatures of about 70 $^\circ$C. The exact temperature and the duration of the process may vary, treatment times are usually in the range from 30 minutes to several days. In the nomenclature, the thermally treated phase is indicated by an index ”$T$”, sometimes also ”$t$”.

7.2.2 Electronic Properties of $\alpha$-(ET)$_2$I$_3$

The untreated $\alpha$-phase undergoes a metal-insulator transition at 137K. At temperatures above 137K, the transport behaviour is approximately metallic, whereas below this transition temperature, the compound is a dielectric insulator. [50][117][12].
CHAPTER 7. INVESTIGATIONS ON $\alpha_T$–(BEDT-TTF)$_2$I$_3$

Figure 7.1: Resistivity versus temperature for different crystallographic phases of (ET)$_2$I$_3$. The different phases are written next to the curves. Note the drastic change when changing the $\alpha$– to the $\alpha_T$–phase. From [83].

7.2.3 Electronic Properties of $\alpha_T$–(ET)$_2$I$_3$

After thermal treatment, the electronic properties of the compound are drastically changed: it is now a metallic conductor down to $\sim$7K, where it undergoes a superconducting transition. This phase is stable, re-heating to room temperature and re-cooling show once again the behaviour as described [10][83]. This drastic change of the electric transport properties is illustrated in figure 7.1.

7.3 Torque Magnetisation Experiments

A large number of samples having undergone different thermal treatments have been examined by the torque method. The leaf spring used in these experiments was made of copper-beryllium bronze, had a thickness of 25 $\mu$m and a shape as shown in figure 3.3. Only in few cases, a signal differing significantly from the background noise and parabolic background magnetisation was detectable. Very low temperatures of about 25mK, which required the use of a dilution cryostat, were necessary to obtain all cases discussed in the following.

7.3.1 Results on Two Samples, Feature at about 10T

One of the most spectacular results is shown in figure 7.2.

The curve represented as a straight line in figure 7.2 was obtained using a sample that had been kept at a temperature of 70 °C during 3 days in air. The dotted curve in figure 7.2 shows the result of an attempt to reproduce this curve using another sample. This latter sample was prepared by keeping the crystal at a temperature of 75 °C during 3 days in a N$_2$ atmosphere.

Although the curve was not reproduced as a whole, it is visible that the comparison curve shows a feature in the region of 10T as it was seen in the initial measurement.
Figure 7.2: Torque Magnetisation signal of $\alpha_T$(ET)$_2$I$_3$ at zero angle with respect to the magnetic field. Straight line: The used sample was kept at 75 C for 3 days. The torquemeter was located about 5 cm above the centre of the magnetic field so that a field gradient occurred across it. Note the different behaviour of up and down sweep direction. The dotted curve shows a signal obtained by using another sample.
There is a pronounced hysteresis in both curves with the general tendency of more pronounced "bumps" during the downsweep than in the upsweep. Starting another upsweep immediately after a downsweep has completed reproduces a curve similar to the downsweep curve that has been measured just before. Waiting for about 10 to 30 minutes then reproduces a curve that is closer to the initial upsweep curve.

All these features could only be observed when the torquemeter was not positioned in the exact field centre, but about 5cm off the field centre, resulting in a field gradient of about $2 \times 10^{-4} \text{T/m}$.

### 7.3.2 Question of Periodicity

Figure 7.3 shows the same data as figure 7.2, but plotted as a function of the inverse magnetic field. Neither in the plot itself nor in the Fourier transform (figure 7.4) there is any obvious periodicity of the magnetisation.

### 7.3.3 Apparent Periodicity in another Sample

However, a third sample showed signals of the type shown in figure 7.5. Apparently there is some periodicity at least at the high field end. Due to this observation, a series of measurements at different angles with respect to the magnetic field was carried out and Fourier transforms have been calculated for each of them. The result is shown in figure
7.6. This sample also underwent a thermal treatment at 75 °C during 3 days.

The analysing procedure has been done separately for the upsweeps and the downsweeps to consider a possible dependence of the spectrum on the observed hysteresis.

In general, three frequency ranges with an enhanced occurrence of frequency components can be observed: one around 50T, the second around 170T and the third around 300T. The very low frequency leads to a very small number of periods within the accessible magnetic field range and therefore the accuracy of the frequency analysis is rather low. Therefore, it cannot be justified to conclude a slight decreasing tendency for the 300T-frequency with increasing angle and an increasing tendency for the 50T-frequency as it could be suggested by the low angle data of the upsweeps. The downsweep data does not suggest any kind of tendency.

The experimental evidence is only sufficient to show the occurrence of frequency components scattering around about 50T, 170T and 300T without any clearly visible dependence on the angle of the sample with respect to the magnetic field.

7.4 Investigations Using an Electron Beam Microscope

7.4.1 Attempt to Realise a Ballistic Electron Focusing Experiment

Basics

The technique of ballistic electron focusing is able to yield additional information about the Fermi surface of the examined system. Whereas data obtained by magneto quantum oscillations mainly gives information about the minima and the maxima of the Fermi sur-
Figure 7.5: Torque magnetisation of another sample tempered at 75 °C during 3 days.

face as it was discussed in the theory part of this work, i.e. the zeroes of the first derivative of the Fermi surface in $\vec{k}$-space, electron focusing is able provide information mainly about the zeros of the second derivative as the observed current density $\vec{j}$ is proportional to the Gaussian curvature $g$ of the Fermi surface

$$\vec{j} \propto \frac{\vec{v}(\vec{k})}{g(\vec{k})}$$

and thus becomes singular in case of one of the Gaussian curvature becoming zero, i.e. the second derivative of the Fermi surface becoming zero along one of the main curvature radii.

The experiment consists mainly of creating a hot spot by the otherwise cooled sample in a small area. Thus, a thermoelectric current is created. If the mean free path of the specimen is sufficiently large, this current propagates ballistically through the sample and the anisotropic current distribution typical for the Fermi surface of the system examined can be detected by scanning the current distribution in real space.

The theory this technique is based on calculations by Kosevich [59], an extensive review of theory and experimental methods and results can be found in [41] and references given therein.
Figure 7.6: Frequencies on an inverse magnetic field scale found by Fourier transforms carried out on the results of torque magnetisation measurements performed at different angles with respect to the magnetic field.
Special Arrangements

The technique of electron focusing requires a mean free path that is excessive by the standards of usual crystal qualities. This is due to the fact that there must be a path ballistically travelled considerably longer than the spatial resolution of the experimental set up which is basically limited by the diameter of the heated excitation zone - the so-called hot spot - and the diameter of the detector. Whereas the latter is typically a point contact with a diameter of about \(1\mu m\), it is the former that imposes the main restriction on spatial resolution. In standard experiments using heating by light, the hot spot diameter is about \(20\mu m\) requiring mean free paths in the range of several \(100\mu m\). This is out of the range that can be realistically expected in an organic conductor sample at the present state of preparation technique.

Therefore, the sample was mounted in an electron beam microscope to provide the heating by the electron beam that can be focused more narrowly than light transported by an optical fibre.

An sketch of the set up is shown in figure 7.7.

Results

The attempts to observe ballistic electron focusing suffered from several experimental problems that were mainly connected with creating a point contact on the sample surface. The concept was to use a second piece of \(\alpha_T-(ET)_2I_3\) contact material. By means of a three dimensional motor driven manipulator within the vacuum chamber of the electron microscope, this piece of material was pressed against the surface of the sample. Then, a short pulse of high current (\(\approx 0.1A\)) was passed through the sample and the detection contact in order to create some sort of welding between the two pieces at the touchpoint. This welding proved to be very difficult, probably because of remaining oxidation products on the surfaces of the pieces of conducting material originating from the tempering process.

However, in some cases, it was possible to create a contact between the two of them. One of these successful attempts is shown in figure 7.8.
Figure 7.8: Successful attempt to create a welded contact between sample and detector contact at room temperature. The image shows the collector contact current in grayscale coding as function of the electron beam position.

Figure 7.9: Attempt to create a welded contact at low temperature (≈ 14K). Again, the image shows the collector current as function of the beam location in grayscale coding.
CHAPTER 7. INVESTIGATIONS ON $\alpha_T$-(BEDT-TTF)$_2$I$_3$

Figure 7.10: Electron beam microscope images of $\alpha_T$-(ET)$_2$I$_3$. The panels show the same region of the sample at different scales. A scale is given in each panel.

The bright zone that can be seen in of figure 7.8 indicates that it was in fact possible to create a detectable current by heating using the electron beam at room temperature. However, the high temperature indicates the non-ballistic nature of the signal. With respect to the experimental resolution, the mean free path is not sufficiently long to observe ballistic features. Attempts to repeat this at low temperatures produced only very high ohmic contacts which did not yield any non-trivial feature in the potential distribution, an example is shown in figure (7.9). Additional information about the Fermi surface according to the intention of this experiment could therefore not be obtained.

7.4.2 Imaging of the Surface

The electron beam microscope was also used to obtain images of the surface of the $\alpha_T$-(ET)$_2$I$_3$ specimens. Two images are shown in figure 7.10.

The upper surface of the depicted specimen is of flat apparence whereas the front surface shows a grainy structure with almost spherical grains of about 1$\mu$m to 3$\mu$m in diameter. The flat surface corresponds to a surface that was created as a natural surface of the initially grown crystal of $\alpha$-(ET)$_2$I$_3$ and was left unchanged after the tempering process. The front surface is not a naturally grown surface, here, the specimen broke off. Thus, the front surface provides an insight to the bulk of the specimen while the upper surface shows the state of a grown surface after thermal treatment.

7.5 Discussion

7.5.1 Isotropy of the Magnetisation, Crystallites

Non-trivial features in the magnetisation were visible only when the magnetometer was placed off the field center. This indicates that the observed dependencies of the magnetisation as function of the magnetic field are isotropic according to equation (3.2). The shape of the measured magnetisation changed as function of the angle, however, no significant dependence of the frequency spectrum as function of the angle with respect to the mag-
netic field could be observed. Both observations suggest that the anisotropic character of the initial compound $\alpha$-(ET)$_2$I$_3$ is generally not preserved in the tempering process.

The observation of the grainy structure in the electron beam microscopy images suggests that the change from $\alpha$-(ET)$_2$I$_3$ to $\alpha$T-(ET)$_2$I$_3$ during the tempering process does not occur homogeneously over the whole sample volume but happens in some kind of bubbles. One can think of the transformation first occurring at some small and spatially very limited locations in the initial $\alpha$-(ET)$_2$I$_3$-crystal and then extending from these centres into adjacent regions of the sample volume until the boundaries of the bubbles touch each other and result in the grainy or spongy structures visible in the electron microscopy images.

In this case, the tempering process would not generate a homogenous single crystal of $\alpha$T-(ET)$_2$I$_3$ even though the piece of $\alpha$-(ET)$_2$I$_3$ at the base of the process was a single crystal before tempering. The $\alpha$T-(ET)$_2$I$_3$ specimen generated by this procedure should then rather be regarded as an accumulation of a large number of crystallites.

### 7.5.2 Orientation of the Crystallites

These crystallites now are not necessarily orientated in the same direction so that averaging macroscopic observables as for example the magnetisation over a large number of crystallites would result in a statistically isotropic average. This could explain the observed isotropy of the magnetisation.

Asking for the nature of the observed features in the magnetisation, two possible explanations spring into mind: phase transitions and quantum oscillations. As it concerns the first, previous work does not indicate any phase transition in $\alpha$T-(ET)$_2$I$_3$ except for the superconducting phase transition itself whereas for a signal as complicated as the ones shown in figure 7.2 or in figure 7.5, several subsequent phase transitions would be necessary. The possibility of explaining the observed features as resulting from a series of phase transitions is therefore regarded as unlikely.

### 7.5.3 Quantum Oscillations from Polycrystalline Samples

Quantum oscillations should not be expected from a polycrystalline sample because of the short mean free path and the stochastic orientation of the crystallites. However, there is a possibility that quantum oscillations might occur even in disorientated polycrystalline systems: if the cyclotron radius is smaller than the extension of a crystallite, i.e. electrons can move within the crystallites without scattering, the magnetisation of every single crystallite can contain contributions being due to magneto quantum oscillations. In the experiment, however, it is impossible to observe a single crystallite separately, the measured magnetisation is always the sum of a large number of crystallites. As a result of the stochastic orientation of the crystallites, all these oscillatory contributions interfere at arbitrary frequencies and phases and should therefore be expected to cancel each other.

In fact, most oscillations in fact do cancel out, but in [90], Shoenberg presents an argument showing that contributions originating from crystallites being close to extremal orientations, i.e. orientations that correspond to a minimum or a maximum of the magneto quantum oscillation frequency as a function of the angle with respect to the magnetic field, may survive at a detectable amplitude because their oscillations have a sufficient residual phase coherence not to cancel out completely. Like this, magneto quantum oscillations in polycrystalline Cu ([90], p. 419 and reference there), Na and Li [77][78] could be observed.
In such a case, the frequency spectrum would not depend on the orientation of the crystal too much as the orientation distribution over the whole sample volume should be statistically homogeneous, as it is the case for the observed signals at different orientations of the sample with respect to the magnetic field, see figure 7.6.

Interpreting the observed features as such residual observations of a polycrystalline material would mean that there is three extremal magneto quantum oscillation frequencies when varying both angles of a crystallite in real space with respect to the magnetic field: 50T, 170T, and 300T.

7.5.4 Comparison to the β-phases

Using this hypothesis, it seems to be worth to make some comparison with the experimental results on β-(ET)$_2$I$_3$, the phase obtained by applying high pressure to β-(ET)$_2$I$_3$ as a strong similarity between the properties of these two phases was already noted when the α$_T$-(ET)$_2$I$_3$-phase was first discovered [10]. Later experimental studies also confirmed the existence of similarities between α$_T$-(ET)$_2$I$_3$ and β-phase, ET-based organic conductors and superconductors by various methods such as ESR, NMR, static susceptibility, electric transport, Raman scattering and infrared absorption [85] [57] [84] [68] [67].

Wosnitza [113] reports results on both phases of the β-phase, the low-$T_c$, low-pressure β$_L$-phase as well as the high-$T_c$, high pressure β$_H$-phase.

For the β$_H$-phase that has a superconducting critical temperature similar to that of the α$_T$-phase, a $1/\cos \theta$ dependence of the main frequency is reported with $F = (3805 \pm 10)\text{T}$ at $\theta = -4^\circ$ with a beating of $\Delta F \approx 57\text{T}$. The fundamental frequency differs by about one order of magnitude from the frequencies found in the α$_T$-(ET)$_2$I$_3$-magnetisation experiments.

Concerning the β$_L$-phase, Shubnikov-de Haas oscillation data are reported in [113] as well as in [53] and [63] at a frequency of about 110T, which matches better the order of magnitude of the frequencies observed in the α$_T$-(ET)$_2$I$_3$-experiments than the values of the β$_H$-phase.

7.5.5 Question of Reproducability

Nevertheless, the ideas discussed here must be regarded as highly speculative. The exact reproduction of a result obtained on one sample using another one was not possible. If the above hypothesis is correct, this is not surprising because the observed behaviour will depend on the individual sample, its crystallite structure etc. Moreover, the properties of one specific sample cannot be regarded as invariant from one cooling cycle to another. The samples are extremely fragile and many of them cracked during the experiments, so that in many cases the sample could not be used any more after one cooling cycle.

The appearance of a pronounced feature in the region of 10T in two different samples may be interpreted such that the orientation distribution of the crystallites is perhaps not completely arbitrary but follows some tendency that might be given by the initial anisotropic structure of the α-(ET)$_2$I$_3$-crystal before the tempering process.

7.5.6 Hysteresis

The apparent hysteresis between up- and downsweeps remains to be explained. Maybe, the interaction of the magnetisation and the external field yields to some ordering of
the grains that in the context of the extreme fragility of the samples could even be of a mechanical nature and that relaxes during some time that the sample is not exposed to an external field.

7.6 Summary and Conclusion, Outlook

A large number of differently treated samples of $\alpha_{7/(ET)}^2\mathrm{I}_3$ has been examined by the torque magnetisation measurement method as well as by electron beam microscopy. Non-trivial magnetisation features could only be observed when a field gradient was present at the position of the torque magnetometer. The samples showing non-trivial magnetisation features were exposed to a temperature of about $75^\circ\mathrm{C}$ for about 3 days, so that these latter parameters might be regarded as favourable for the occurrence of such features.

The magnetisation results on one sample could be separated into three frequency components on a $1/B$-scale. The observed frequencies scattered around 50T, 170T and 300T. No significant dependence of these frequencies as function of inclination angle of the sample with respect to the magnetic field could be observed.

The apparent isotropy of the magnetisation features, the apparent independence of the oscillation frequencies of the inclination angle and the grainy structure observed by electron beam microscopy leads to a speculative interpretation of the observed features as magneto quantum oscillations of a polycrystalline material. Comparing the observed frequencies in this context to known data about the $\beta$-phases of this compound seems to indicate a closer similarity to the $\beta_L$-phase than to the $\beta_H$-phase.

Attempts to observe ballistic electron focusing in the $\alpha_{7/}(ET)$-phase failed.

The polycrystalline structure of the material and its extreme fragility represents a significant experimental problem, especially the reproducability of results suffers from it.

Although some hints for the existence of at least one low quantum oscillation frequency $\leq 300\mathrm{T}$ have been found, the evidence cannot be regarded as conclusive. For further investigation, it appears to be imperative to find a way to prepare a single crystal of sufficient volume of the $\alpha_{7/}(ET)$-phase or at least a sample consisting of much larger crystallites than the ones used for the experiments described in this chapter.
CHAPTER 7. INVESTIGATIONS ON $\alpha_T$-(BEDT-TTF)$_2$I$_3$
Chapter 8

Experimental Quantum Oscillation Study of the Heavy Fermion System CePd$_2$Si$_2$

8.1 Presentation of the System

8.1.1 General Properties of Heavy Fermion Systems

The so-called heavy fermion systems are a particular class of strongly correlated electron systems. Their name stems from the occurrence of unusually high effective masses of the conduction electrons, which can reach values of as high as a few hundred electron rest masses. Their thermodynamic and transport properties at low temperatures differ significantly from those of normal metals. In many cases they can however be described by a Fermi liquid model. Nevertheless, in some particular conditions, these systems can exhibit non-Fermiliquid behaviour as well.

One of the most prominent properties of such systems is the apparent co-existence of magnetic order and superconductivity in some compounds [27][32].

8.1.2 The Occurrence of High Effective Masses

Heavy fermion systems are intermetallic compounds based on cerium (Ce), uranium (U) or ytterbium (Yb). All these elements belong to the rare-earth elements of the periodic system. Although these elements have 5$d$- and 6$s$-electrons, their outer shells are not filled up with electrons with increasing element number within the series, but the 4$f$-shell is successively filled up. In the case of uranium, this role is taken by the 5$f$-electrons. In the following, the term $f$-electrons will mean 5$f$-electrons in the case of uranium and 4$f$-electrons in the other relevant cases, i.e. the elements of the lanthanide-series. Usually, the outer 5$d$- and 6$s$-electrons provide efficient screening of the $f$-electrons preventing them from interactions. Consequently, in almost all situations all Lanthanides possess the chemical valence $3^+$, independently of their order number.

In some lanthanides such as cerium the screening of the $f$-electrons is less efficient. Cerium possesses only one $f$-electron whose wave function is relatively extended in real space thus allowing for hybridisation with valence electrons of the ligands. The strength
of this hybridisation $g$ now determines the localisation of the $f$-electrons. For small values of $g$, the $f$-electrons are well localized and the interaction of the magnetic moments of the cerium atoms in the crystal lattice leads to a magnetically ordered phase at low temperatures. With increasing $g$, the localisation decreases and allows the $f$-electrons to "hop" from one atom to another. At some critical value $g_c$, the magnetic order disappears completely and the $f$-electrons become totally delocalised; they then move freely and act as conduction electrons.

Heavy fermion systems can be found in the transition regime where the magnetic order disappears. The interaction between $f$- and conduction electrons leads to strong correlations of the latter because they cannot move independently anymore. This leads to a strong increase of the effective mass of the conduction electrons, which in a pictorial way can be seen as due to the slow motion of $f$-electrons through the crystal lattice [27].

8.1.3 Kondo Interaction and Increase of Quasiparticle Density of States

The situation in a heavy fermion system can be treated more formally by regarding the effect that magnetic impurity in a metallic crystal has on the conduction electrons. Such a situation was first considered by Kondo [58] in order to explain anomalies in the resistivity of some certain metallic systems at low temperatures as the result of magnetic scattering at these impurities. This can be shown to be the cause for the occurrence of a sharp resonance in the quasiparticle density of states, the so-called Abrikosov-Suhl resonance [3][94] that accounts for the high effective mass and other specific properties of heavy fermion systems. This sketch of the relevant argument follows the representation in [32].

The basic idea of the model is that the local magnetic moment is screened by spin polarisation of the surrounding conduction electrons. Using Friedel's sum [26] in the most general form as given by the Fermi liquid theory, the total number of localised electrons $n_l$ can be expressed in terms of the scattering phase shifts $\delta_\alpha$ characterised by local quantum numbers $\alpha$ as:

$$n_l = \frac{1}{\pi} \sum_\alpha \delta_\alpha.$$  \hfill (8.1)

The quasiparticle density of states $N_\alpha$ at the Fermi level $E_F$ for the channel characterised by $\alpha$ can be expressed by

$$N_\alpha (E_F) = \frac{1}{\pi \Delta_\alpha} \sin^2 (\delta_\alpha)$$  \hfill (8.2)

[62][36] with $\Delta_\alpha$ being given by the self energy of the localised electrons $\sum_\alpha (E_F + i\eta) = R_\alpha - i\Delta_\alpha$. Combination of equations (8.1) and (8.2) gives a direct relation between the quasiparticle density of states at the Fermi level $N(E_F)$ and the number of localised electrons $n_l$:

$$N (E_F) = \frac{1}{\pi \Delta} \sin^2 \left( \frac{\pi n_l}{2} \right).$$  \hfill (8.3)

In heavy fermion systems, $n_l$ and $\Delta$ are such that a sharp peak of $N(E)$ occurs close to $E_F$ resulting in high effective masses, see equation (1.13).
8.2. MOTIVATION

8.1.4 Magnetic Susceptibility

Whereas in normal metals the Pauli susceptibility \( \chi = \mu_0 \mu_0^2 N(E_F) \) is almost independent of the temperature, heavy fermion systems exhibit a strong increase of \( \chi \) towards low temperatures being due to the increase of \( N(E_F) \) \[99\].

8.1.5 CePd\(_2\)Si\(_2\) in Particular

CePd\(_2\)Si\(_2\) crystallizes in a body-centered tetragonal structure (space group I\(_4\)/mmm). It belongs to the family of CeM\(_2\)T\(_2\) heavy fermion compounds where M is a transition metal and T = Si, Ge. An antiferromagnetic transition with \( T_N \approx 10 \text{K} \) with a static moment of \( 0.6 \mu_B \) is known. The magnetic moments are aligned along the [110] crystallographic direction. A Sommerfeld coefficient of \( \gamma \approx 100 \text{mJ/mole} \) is extrapolated from the paramagnetic regime \[104\].

8.1.6 Heavy Fermion Systems in High Magnetic Fields

As already mentioned, a high magnetic field tends to weaken the many-body interactions that result in the occurrence of high effective electron masses in heavy fermion systems. A theory of the de Haas-van Alphen effect in strongly correlated electron systems with special attention to heavy fermion systems has been worked out by Wasserman \[107\] \[106\].

When considering the Zeeman splitting of the \( f \)-levels, a field-dependent effective electron mass results:

\[
m_{\text{eff}} = m_{\text{eff}}^0 \left(1 + \frac{2Dn_fT_K}{N(T_K + Jg_f\mu_BB)^2}\right)
\]

where \( T_K \) is the Kondo temperature of the system, \( 2D \) the unrenormalised conduction bandwidth, \( n_f \) the mean occupation number of the \( f \)-level, \( g_f \) the \( f \)-level \( g \)-factor, \( N = 2J + 1 \) the \( f \)-level degeneracy and \( m_{\text{eff}}^0 \) the effective electron mass without considering the many-body interactions.

8.2 Motivation

The particular interest in CePd\(_2\)Si\(_2\) arises from its superconductivity. Superconductivity was first found in a small pressure range around the quantum critical point where the antiferromagnetic ordering temperature vanishes \[105\]. This observation gave rise to the hypothesis that this superconductivity may be caused by magnetic pairing of the electrons instead of the phononic BCS-mechanism. Several later studies could not confirm the existence of superconductivity, although Raymond and Jaccard \[80\] \[79\] could confirm it, but in a considerably wider pressure range than in \[105\]. Recent high pressure studies again confirmed the existence of superconductivity \[88\] \[23\].

Another important motivation for the experiments described in this chapter was the question if this compound shows a dependence of the effective electron mass as function of the field. Such a dependence has been observed for example for CeB\(_6\) \[49\]. Physically, such a change of the effective mass can be understood by breaking the interaction between the \( 4f \)- and the conduction electrons. The system CePd\(_2\)Si\(_2\) seems to be particularly
suitable for such an experiment since its Kondo temperature $T_K$ is about 10 K, which is quite low among the heavy fermion systems. As it can be seen from equation (8.4), a low Kondo temperature $T_K$ should favour a pronounced field dependence of the effective electron mass.

Moreover, in order to shed some light onto electronic and especially the superconducting properties of the system, it was of interest to obtain experimental information about the spectrum of observable quantum oscillation frequencies. These results were to be compared to the existing bandstructure calculations [38].

8.3 Experimental Results

8.3.1 Experimental Conditions

A high quality single crystal of CePd$_2$Si$_2$ was mounted on a leaf spring to measure the magnetic torque as described earlier in this work. The dimensions of the used sample are 600 x 150 x 75 $\mu$m$^3$. The spring was made of 25 $\mu$m thick CuBe. The orientation of the sample was $\vec{H} \parallel \vec{a}$ for the zero degree position. Tilting with respect to the magnetic field at low temperature and in situ was possible. This orientation was chosen because test had shown that here the smallest background magnetisation could be expected. Background magnetisation is quite strong in this compound due to its antiferromagnetic properties. The measurements were carried out in the M6 magnet of the Grenoble High Magnetic Field Laboratory, allowing for a maximum field of 23 T. Some runs were made on magnet M9 (28 T maximum field). A dilution cryostat (Oxford Instruments) has been used to obtain temperatures as low as 30 mK.

8.3.2 Kink at about 10T

A kink in occurring in the background magnetisation at about 10T was found. This kink is attributed to the metamagnetic transitions that has already been found in temperature-dependent measurements of the resistivity in the same field range [87], for an example see figure 8.1.

8.3.3 Angular Dependence of the Oscillation Frequencies

A systematic survey of the spectrum of dHvA frequencies has been done in the angular range from 0° to 45° so that the range from $\vec{H} \parallel [100]$ to $\vec{H} \parallel [110]$ was covered. As an example, figure 8.2 shows the oscillatory magnetisation for an inclination angle of 7.5°. Non-oscillating contributions have been subtracted. A fast Fourier transform of the same set of data is shown in figure 8.3.

Such data has been taken for several angles between 0° and 45°. The frequencies found are shown in figure 8.4.

The observed frequencies have been sorted in ten groups labeled from I to X in figure 8.4. In the angular range from 0 to 22.5 °, series IV is the one with the most pronounced amplitude. At low angles, it is split, split frequencies could be observed at 0° and 2.5° and are shown as series V. The second harmonic of IV could also be observed, it is shown as series VII. At higher angles, series IV disappears and series III takes the role of the main - i.e. most intense - frequency. Generally, there is a minimum of all the amplitudes around
Figure 8.1: Kink observed in the torque magnetisation of CePd$_2$Si$_2$ that is attributed to a metamagnetic transition.
30°. A splitting of the series VI frequency at 0° seems to be correlated with the field: the lower splitting frequency - shown as series X - appears at higher fields while the higher one at lower fields. Series IX could be observed at high fields only. In the sweeps up to 23T, it was hardly visible at all, whereas in the sweeps up to 28T, its existence becomes evident. The behaviour at low frequencies - series I, II, and VIII - is not quite clear. Several frequencies interfering with each other were found there, but they could not be clearly resolved in any case. Most probably this is due to the fact that the limited field range contains only relatively few periods of the low frequency oscillations. The frequencies as shown for series I, II, and VIII in figure 8.4 are therefore to be regarded rather than a sketch whereas the existence and dependence of the higher frequencies as shown is quite clear.

8.3.4 Field Dependence of the Effective Electron Mass

At 0° and 7.5°, sweeps have been made at different temperatures allowing for an analysis of the effective electron mass directly from the dHvA data as described earlier in this work. At 0°, data has been taken at 30mK, 80mK, 120mK, 160mK, 200mK, 250mK, 300mK and 400mK, at 7.5° at 35mK, 80mK, 120mK, 160mK, 200mK, 240mK, 280mK, 320mK, 360mK, 400mK, 440mK and 480mK. For each temperature, m the Fourier amplitude of the main frequency (series IV) was computed over the same 1T windows, which were moved through the whole data range with a step of 0.5T. The results for the two angles are shown in figures 8.5 and 8.6. The other series were not regarded for an effective mass analysis.

Figure 8.2: Oscillatory torque magnetisation for CePd$_2$Si$_2$ at an inclination angle of 7.5° and a temperature of 35 mK.
8.4. DISCUSSION

since their amplitudes are quite low compared to series IV. The separation of several small windows of the field implies a further reduction of the accuracy for the effective mass, therefore it was desirable to have an amplitude as high as possible for this analysis. The series IV frequency at 7.5° has the highest amplitude of all frequencies in the observed angular range.

At both orientations, a field dependence of the effective electron mass is clearly visible. Up to about 17T, the mass decreases monotonously, but has a local maximum around 20T...21T. At still higher fields it comes down again so that at about 22T, it has once again roughly the same value as it had around 17T...19T. Although the guides for the eyes in figures 8.5 and 8.6 seem to indicate a further decrease after the said local maximum, this cannot be said without more data at higher fields. It might also be possible that the mass saturates at even higher fields.

8.4 Discussion

8.4.1 Bandstructure Model

Figure 8.7 shows the spectrum of dHvA frequencies predicted by the already mentioned theoretical model [38]. The corresponding predicted Fermi surface is shown in figure 8.8.

Comparison with figure 8.4 shows a qualitative correspondence, without an exact matching of the numbers: series IV/V of the experimental results can be associated with series E and F of the model, even the splitting at low angles is matched. However, the
Figure 8.4: Angular dependence of dHvA frequencies in CePd$_2$Si$_2$. The angular range covers the orientations from [100] to [110].
Figure 8.5: Field dependence of the effective electron mass in CePd$_2$Si$_2$ at an orientation of 0°. Frequency of series IV in figure 8.4. The line is a guide for the eyes.
Figure 8.6: Field dependence of the effective electron mass in CePd$_2$Si$_2$ at an orientation of 7.5° from [100] towards [110]. Frequency of series IV in figure 8.4. The line is a guide for the eyes.
Figure 8.7: Spectrum of dHvA frequencies of CePd$_2$Si$_2$ as predicted by the model [38].
Figure 8.8: Fermi surface as predicted by Harima [38].
theory predicts a frequency range of about 1500T to 2500T while the experiment locates
this series in the range 3500T to 4300T. Disregarding series IX for a moment because it
seems to appear at high fields only, series B of the model can be associated with VI/X of
the experimental results. Here, the theory predicts an order of magnitude of 10000T for
the frequency while the experiment shows about 5000T. The low frequency regime - series
I,II and VIII and G,H and I - is difficult to compare due to the already mentioned difficul-
ties in resolving them in the experiment. However, the model predicts here three different
series and the experiment seems to indicate several frequencies close to each other. The
order of magnitude of the frequencies of about 1000T is roughly the same for both theory
and experiment. Regarding the angular range, D might well be associated with III, but
the theory predicts it at 3000T to 10000T and at frequencies higher than those of E/F,
while in the experiment it appears at about 2500T and thus lower than the corresponding
series IV/V. Nothing that could correspond to series A and C could be observed in the
experiment.

Qualitatively, there are many similarities between the theoretical prediction and the
experiment, however, the numbers do not match. The theory therefore seems to predict a
Fermi surface of roughly the correct shape, but not of the correct dimensions.

This might be explained by the observation of a probably metamagnetic phase transition in the field range of approximately 9...10 T of which

8.4.2 Decrease of the Effective Electron Mass

The initial decrease of the effective electron mass in the field range up to 17T is consistent
with experimental observations in other heavy fermion systems \cite{49} as well as with the-
toretical models \cite{108}. As mentioned in the introduction, this is associated with breaking
the coupling of the conduction electrons with the 4f-electrons.

8.4.3 Feature at 21T, Suspected Transition

The local maximum of the effective electron mass around 21T cannot be explained within
the context of the theoretical ideas mentioned. The feature occurs at about the same field
for both orientations, for which an effective mass analysis was done. Moreover, there are
subtle changes in the dHvA frequency spectrum that occur around the same frequency:
the series IX in figure 8.4 is much clearer to see in higher fields from about 20T onwards,
the 0° degree frequency of series VI seems to be another at low fields than at high fields,
also apparently from about 20T onwards. It is difficult to say if they really only occur at
fields higher than 20T and how pronounced the change really is because at the time of
writing this thesis, there is only systematic data available for the range of up to 23T. In
the regime of higher fields, up to 28T, only preliminary measurements have been made.
These, however, show the said changes quite clearly, but still have to be confirmed in a
systematic study. Both phenomena give rise to the suspicion of a magnetically induced
transition around 20T...21T that might slightly effect the bandstructure and consequently
the spectrum of dHvA frequencies.

The nature of this transition is however unclear. Available data on the resistance as
function of the temperature \cite{87} show just one transition around 10T that is usually held
to be metamagnetic. This would mean that the high field transition would be a new and
hitherto unknown one.
The appearance of series IX and X at high fields should not be overestimated either. Knowing that the system incorporates effective electron masses that decrease with higher fields, this effect alone could give rise to the appearance of further frequencies at high fields because the drastic increase of amplitude caused by both decreasing effective mass and increasing field (c.f. equation (1.11) and its amplitude factors) could simply make it appear by rising it over the noise level only at high fields. It is also not impossible that magnetic breakdown might play a role in generating this frequency. Nevertheless, all these effects cannot account for the local maximum of the effective electron mass as function of the field at roughly the same field where these frequencies appear. If this is pure coincidence or has some physical meaning is one of the questions that must be cleared in a systematic study at even higher fields.

8.5 Summary, Conclusions, Outlook

This chapter describes an experimental dHvA study on CePd$_2$Si$_2$ using the torque method. As a summary, result and outlook, the following findings can be stated:

- The spectrum of dHvA frequencies has been recorded in the range from [100] to [110] orientation of the magnetic field. Comparison with the theoretical model [38] shows qualitative consistency between theory and experiment, but lacks quantitative agreement.

- At 0° and 7.5° orientation, a field dependence of the effective electron mass could be observed. The mass first decreases in accordance with existing theoretical models, but then shows a local maximum around 20T...21T, which cannot be accounted for by the said models.

- Together with the local maximum of the effective electron mass, changes in the dHvA frequency spectrum could be observed. If and how these effects are related must remain as the subject of studies in the future, but together these two effects give rise to suspecting a magnetically induced transition of so far unknown nature.

- In the range of about 9...10 T, a kink in the magnetic background as function of the field could be observed. This can be associated with a transition observed in resistivity measurements in the same field region, probably, the transition is of metamagnetic nature.

Further studies on the compound should try to clear these matters. Studies at higher magnetic fields seem to be compulsory for this purpose to get more data above the suspected transition. Moreover, a high field study could also help to reveal the true behaviour of the dHvA spectrum at low frequencies by providing more periods within the set of data when the sweeps are started at relatively low field. Even the possibility of a pulsed-field experiment should be examined for this purpose, although it poses the problem of running a dilution cryostat in a pulsed field, which is likely to cause problems with keeping the temperature constant and maintaining very low temperatures. Nevertheless, it is not impossible in principle.
Moreover, the measurement of other parameters, notably the isotropic magnetisation as a function of the magnetic field and temperature is desirable. This should help to figure out the nature of the system’s ground states in between the observed magnetically induced phase transitions. Measurements of the specific heat might also contribute to this. Knowing the appropriate ground states would then also help to improve the bandstructure calculations.
STUDY OF CePd$_2$Si$_2$
Chapter 9

Vortex Dynamics Effects in Superconducting Niobium

9.1 Introduction

9.1.1 Generalities

As shown in the theory part of this work, the usual equilibrium state of a type-II- superconductor below critical temperature and at a magnetic field $H_{c1} < H < H_{c2}$ is the regular and periodic Abrikosov vortex lattice structure as shown in figure 2.1. Far from equilibrium, however, different stable or metastable structures may be formed. This chapter presents experimental results on superconducting niobium placed in a magnetic field. A disequilibrium situation is created by periodic heating of the otherwise cooled sample. The applied experimental technique allows to observe the potential distribution on the sample surface as function of position in real space. A ring shaped normal conducting domain around the heated spot is observed, its extension is much larger than the heated zone itself. The ring structure appears to be fixed.

The experimental observations are discussed in comparison with results of numerical calculations performed by B. Shapiro and co-workers [6][7][28]. These calculations are based on time-dependent Ginzburg-Landau theory and the heat conduction equation. They show the occurence of a so-called super-vortex in the heated zone that explosively nucleates vortices that emerge in rings from the heated zone into the sample volume. The observed rings are interpreted as being due to this effect, with the emerged rings fixed by pinning. Due to the pinning, there is no principal limitation to the lifetime of these rings so that they constitute a metastable state of a type-II- superconductor different from the equilibrium Abrikosov vortex lattice.

The theoretical input to explain these structures consists exclusively of time-dependent Ginzburg-Landau theory and classical heat conduction theory. Therefore, the scenario does not only apply to the normal/superconducting phase transitions in type-II-superconductors, but also to other kinds of phase transitions of the second order that can be described by Ginzburg-Landau theory. The effects described in this chapter should therefore not be seen as being limited to type-II-superconductors, but just as one example of the manifestation of the described general scenario, here demonstrated for the example of a type-II-superconductor.

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9.1 Niobium

The superconducting system used for the experiments described in this chapter is niobium. Niobium is the only elementary type-II-superconductor. Because it is an elemental metal, it can be prepared as very high quality single crystals. Its main superconducting properties are as follows:

- Critical temperature at zero field: \( T_c = 9.15 K \) \(^{[24]}\).
- Coherence length \( \zeta = 3.8 \cdot 10^{-8} m \) \(^{[55]}\).
- Penetration depth \( \lambda = 3.9 \cdot 10^{-8} m \) \(^{[55]}\).
- Energy gap \( \Delta \) : see table 9.1.
- Critical fields \( H_{c1} \) and \( H_{c2} \) : see table 9.2.

Niobium crystallizes in a bcc-structure with a lattice constant of \( 3.3 \cdot 10^{-10} m \) \(^{[55]}\). Its electronic configuration is [Kr] 4d\(^4\)5s\(^1\) and the Fermi energy is 9.05 eV \(^{[72]}\).

9.2 Sample Specifications

The sample was grown as a single crystal by the Czochralski method in the Max-Planck-Institut für Metallforschung in Stuttgart, a slab of about 2mm thickness was cut off by spark erosion, the thickness then further reduced to 0.3mm (middle) to 0.15mm (edges) by electrochemical etching. For this latter step, the method of etching was chosen because it does not disturb the crystal structure. A relative resistance ratio (RRR) between room temperature and 4.2K of 2500 was measured. This value indicates a good quality single crystal with still a sufficient number of residual defects to provide pinning centres.
9.3 Experimental Technique

The experimental set up consists mainly of a mechanical micropositioning device [42] that is used to control the position of an optical fibre close to the sample surface as shown in figure 9.1.

The whole apparatus is immersed in liquid $^4$He in a glass cryostat, so that the sample as a whole is continuously cooled and the heating is confined to a small zone in close vicinity to the incident light spot. Experimental findings suggest a hot spot diameter of about 20µm [41].

The light that is coupled into the fibre is generated by an Ar$^+$-ion laser. It is mechanically chopped at a frequency of 100..200Hz, a lock-in amplifier is synchronised with the optical chopper and detects the collector signal. Its intensity and phase is recorded by a personal computer that is also used to control the motors driving the mechanical micropositioning unit and thus the fibre position, see figure 9.2.

The collector contact is made up of wire at the end of which a tip of about 1µm diameter is produced by means of electrochemical etching. Before the actual measurement is started, the contact is pressed against the sample by means of manually operated mechanical actuators. A short pulse of high voltage (about 100V applied via a 1MΩ-resistor in series) is applied to weld the contact to the sample surface. A typical contact resistance is about 1Ω at 4.2K.

9.4 Origin of the Signal

The collector contact records voltage drops between the contact position and the reference contacts at the sample edge. Such a voltage drop can come about as follows:
Figure 9.2: Schematic overview of the experimental set up.
9.5. EXPERIMENTAL OBSERVATIONS

9.5.1 Large Ring Structure

Figure 9.3 shows a potential distribution experimentally observed at a temperature 4.2K and a magnetic field perpendicular to the depicted sample surface of 0.1T. The collector contact voltage is shown in grayscale coding and in perspective representation as function of the optical fibre position.

A large bright ring structure of about 500µm in diameter appears around a sharp peak almost but not exactly in its center. The ring structure is not sharp, it appears to be smeared out.

9.5.2 Inner Structure of the Sharp Peak

A close-up scan with smaller distances between measuring points reveals an inner structure of the sharp peak at the approximate centre of the large ring structure. Depending on the

- in normal conducting state: by the voltage drop occurring over the contact resistance when the thermoelectrically excited current traverses the sample
- in the mixed state: as a result of vortex movement according to equation (2.18).
- in the mixed state: voltage drop over the final resistance of the vortex core

The relation of these to possible origins one to each other and their roles in contributing to the observed signal will be dealt with in the discussion part of this chapter.
Figure 9.4: Close-up scans of the small structure approximately in the centre of the structure shown in figure 9.3. Left: at 0.052T, 30x30 data points, signal range -190nV to -150nV, image frame (80µm)$^2$, right: at 0.1T, 20x20 data points, signal range from -210nV to -130nV, temperature for both measurements 4.2K.

magnetic field, either a bright spot (corresponding to a high potential) encircled by a dark ring (corresponding to a low potential) or the inverse can be seen as shown in figure 9.4. The diameter of this small structure is about 30µm and thus only slightly larger than the spatial resolution of the apparatus. Figure 9.5 shows the change from the situation where a low potential spot is encircled by a high potential ring to the inverse as function of the magnetic field. The scanner was used in one direction only, line scans across the small structure were carried out at different magnetic fields. Figure 9.5 shows the fibre position $x$ on one axis and the magnetic field on the other axis. The signal intensity is plotted as the height of the surface shown.

9.6 Numerical Calculations

This section describes the main physical input and the main results of the numerical model calculations that will give the framework for discussing the experimental results obtained
9.6. NUMERICAL CALCULATIONS

Figure 9.5: Linescans across the small ring structure as function of the magnetic field. The signal intensity is shown as the height of the surface represented in the figure.

on superconducting Nb. This presentation follows mainly the one given in [28].

9.6.1 Physical Input to the Numerical Model

The physical input to the numerical model calculations carried out by B. Shapiro and co-workers are the following:

- Time-dependent Ginzburg-Landau theory as stated in equations (2.24), (2.25) and (2.27)
- Classic thermal diffusion:

\[
\frac{\partial \tau(\vec{r}, t)}{\partial t} = D \nabla^2 \tau(\vec{r}, t) + \left( \frac{\partial A}{\partial t} \right)^2
\]

(9.1)

where \( \tau \) is the local temperature at position \( \vec{r} \) and time \( t \), \( D \) the diffusion coefficient and \( \vec{A} \) the vector potential.

9.6.2 Initial and Boundary Conditions

The time-dependent Ginzburg-Landau equations (2.24), (2.25) are solved numerically using the following initial conditions:

- At the beginning \( (t=0) \), a normal spot \( (|\psi| = 0) \) of radius \( R \) with \( n \) quanta of magnetic flux trapped inside exists.
- The magnetic field is uniform across the initial spot and decays outside.
To these initial conditions, the following boundary conditions are added:

- \[ \vec{A}(t)|_{\text{boundary}} = \vec{A}(0)|_{\text{boundary}}, \]  
  \tag{9.2} 
  
  that is the vector potential on the boundary is unchanged at any time.

- \[ \left( \frac{\partial \psi}{\partial \vec{n}} \right)|_{\text{boundary}} = 0, \]  
  \tag{9.3} 
  
  that is the disappearing of the order parameter on the boundary.

The calculation was carried out also for more complicated boundary conditions, but the results have been found to vary only slightly and only close to the boundary. No heating of any part of the system is assumed for times \( t > 0 \), that means essentially that the system after creating the hot spot is essentially left to itself and its relaxation from this initial disequilibrium state into equilibrium is to be simulated.

### 9.6.3 Results of the Numerical Model Calculations

Depending on the exact choice of the initial conditions, Shapiro et al. distinguish between three different resulting scenarios.

- If a strong magnetic field \( H \geq H_{c2} \) is confined in a normal conducting spot of radius \( R \geq \xi \), a supervortex is formed which then decays into single vortices forming an Abrikosov vortex lattice analagously to the supervortex decay in liquid He \[ [8] \].

- In case of a large normal conducting spot (\( R \gg \xi \)) and the field trapped in the spot is \( H > H_{c2} \), the order parameter grows with ongoing time and thus ongoing cooling leaving a regular lattice of zeros, i.e. normal conducting spots, which subsequently relax into the Abrikosov vortex lattice.

- In case of a large normal conducting spot (\( R \gg \xi \)) and the field trapped in the spot is \( H \ll H_{c2} \), a highly unstable state is created. At a first stage, the hot spot shrinks. In a second stage, explosive nucleation of vortices occurs in the spot. Thus, vortices and possibly also antivortices are created. Initially, order-parameter zeroes occur similarly to the case \( H > H_{c2} \), but their density can now be considerably exceed the mean number of flux quanta per unit area so that antivortices must occur in order to conserve the total flux. Most of them annihilate rapidly, but some of them may remain and can emerge from the spot. This scenario is illustrated in figure 9.6.

### 9.7 Discussion

The discussion presented in this chapter is aimed at an interpretation of the experimental observations within the context of the numerical model as it has been presented in the previous section.
9.7. DISCUSSION

Figure 9.6: Scenario of explosive vortex nucleation \((R \gg \xi; H < H_D)\): Results of numerical calculations of (from left to right) magnetic field \(B\), order parameter \(\psi\) and temperature \(T\) at times (a) \(t = 0\), (b) \(2 \cdot 10^{-9} s\), (c) \(1.2 \cdot 10^{-8} s\), (d) \(5 \cdot 10^{-7} s\). The initial spot radius was set to \(R = 4 \cdot 10^{-5} \text{cm}\), the diffusion coefficient \(D = 0.009 \text{cm}^2/\text{s}\) and the initial trapped flux as 16 flux quanta. [86]
CHAPTER 9. VORTEX DYNAMICS EFFECTS IN SUPERCONDUCTING NIOBIUM

9.7.1 Experimental Conditions in the Context of the Model

In the experiment, the chopping of the light provides periodic subsequent heating and cooling of one spot on the sample surface. It can be assumed that this heating is sufficient to reach a temperature above the superconducting critical temperature $T_c$ in the spot. This latter assumption is based on observations on normal conducting metals such as silver under comparable experimental conditions that indicate an energy distribution of the carriers that correspond to a temperature of several tens of K in the hot spot (e.g. [76]). It is thus assumed that during the heating period, i.e. the time the laser light shines onto the sample surface, a normal conducting spot is created.

As for the radius of this normal conducting spot, it is basically determined by the radius of the light spot on the surface. An optical fibre of $15\mu m$ was used in the experiments, accounting for the distance between the fibre and the sample surface as well as for the cone formed by the light emerging from the fibre, a spot radius of $R \approx 1 \cdot 10^{-5}m$ can be estimated. Comparing this to the coherence length $\xi = 3.8 \cdot 10^{-7}m$ [55] shows that the normal conducting spot thus created indeed fulfills the condition $R \gg \xi$.

The magnetic field was kept at $B = 0.1T$ directed perpendicularly to the sample surface. A comparison with the critical fields 9.2 shows that this is well below the second critical field $H_{c2}$. The system can thus be expected to be in the mixed state.

Moreover, within the framework of the numerical model presented, the fulfillment of both of the requirements $R \gg \xi$ and $H < H_{c2}$ leads to the expectation of explosive vortex nucleation to occur.

9.7.2 Time Scales

The experimental time scale is determined by the modulation frequency of the light. Modulation frequencies of about 100Hz were used, with a ratio of 1:1 for the times of maximum intensity and no intensity, corresponding to heating and cooling periods respectively. Consequently, heating and cooling times of about $5 \cdot 10^{-3}s$ result.

One point of data as shown in figure 9.3 has been recorded during an acquisition time of several seconds. It is thus the result of an averaging process in time that extends over several hundreds of heating-and-cooling cycles.

The time scale of the explosive nucleation process is considerably shorter than the time scales of the experimental observations as stated above. According to [28], the shrinking of the normal spot without any vortex nucleation takes about the first $10^{-11}s$ after the heating has stopped. The nucleation occurs during another $10^{-11}s$ to $10^{-10}s$. These time scales are considerably shorter than the time scales of the experimental observation. Therefore, a direct observation of the nucleation process cannot be expected from the experiment, the observed phenomena should rather be regarded as a long-term result of the nucleation.

9.7.3 Length Scales

The spot radius has been estimated to $R \approx 10\mu m$ as stated above whereas the observed large ring structure has a radius of about $400\mu m$. Thus, the large ring structure cannot be associated with the spot itself, its explanation requires the consideration of transport phenomena on a length scale about one order of magnitude larger than the spot diameter.
9.7.4 Nature of the Large Ring Structure

Within the framework of the considerations made in the previous paragraphs of this discussion, the large ring structure is now regarded as the experimentally observed nucleated vortices averaged over several heating and cooling cycles. Moreover, the time scales indicate that the nucleation time itself is negligible compared to the time of observation. The emerging vortices must therefore be fixed in the position they are finally observed. Such a fixing could occur by vortex pinning.

In this interpretation, during the heating period first a normal conducting spot is created. At the beginning of the cooling period, explosive vortex nucleation occurs on the boundary of the normal conducting spot. The vortices created in this process emerge in the sample until they are finally pinned. The RRR of about 2500 indicates a good quality single crystal with however some remaining crystal defects that may act as vortex pinning centres.

Due to the data acquisition time extended over many heating and cooling cycles for each observed point of data, the observed ring is made up as the result of many vortex fronts coming across it. This results in an averaging that manifests itself as the obvious smearing of the ring structure in the experimental observation. The scattering of the vortices and their final pinning are stochastic processes that cannot be predicted with exactness. Thus, the observed large ring structure represents a statistical distribution of the pinned vortices that emerged from the nucleation process on the boundary of the normal conducting spot.

9.7.5 Origin of the Observed Voltage Drop

As it was lined out in section 9.4, there is three possible origins of the signal. The large ring structure is far away from the normal conducting spot compared to the extension of the latter so that only possibilities concerning the mixed state need to be considered.

Here, the voltage drop can either occur as a dynamic phenomenon due to energy dispersion by moving vortices or due to static vortices as a manifestation of their finite core resistivity. The question to be looked at is thus whether the observed voltage drops are created by static or moving vortices.

Assuming first the possibility of moving vortices allows for an estimation of their velocity. Since the nucleation time can be neglected compared to the observation time, the velocity can simply be estimated to an order of magnitude by dividing the average distance they propagated since the end of the heating period, i.e. the average ring radius, by the cooling time:

\[ v_{\text{vortex}} = \frac{r_{\text{ring}}}{t_{\text{cooling}}} \approx \frac{4 \cdot 10^{-4} \text{m}}{5 \cdot 10^{-3} \text{s}} = 8 \text{m/s} \]  

(9.4)

which appears to be rather slow.

Moreover, if the signal were due to moving vortices, there should be considerable voltage drops closer to the excitation location as well because the vortices have to pass these positions. One should expect a disc in the potential distribution, not a ring in the middle of which - with the exception of the excitation spot - the potential appears to be the same as on the outside, but the experimental observation rather indicates the latter
to be the case. For these reasons, the hypothesis that the observed ring is due to moving vortices is regarded as highly unlikely.

Consequently, the signal is regarded as the result of the finite resistivity of static, not moving vortex cores. Pinning provides an explanation how such a demobilisation of the propagating vortices can occur.

9.7.6 Persistence of the Ring Structure, Metastability

It seems to be worth to emphasize that the pinned ring structure can in principle persist without any limitation in time as long as the conditions of magnetic field and temperature remain unchanged. Already in this experiment, it persists during a time that is by about seven orders of magnitude longer than the vortex nucleation time. Thus, it is metastable and the present result is an example of a state that can persist in a type-II-superconductor without limitation in time and that is different from the usual Abrikosov vortex lattice. The final dimension of the ring depends on the initial excitation, especially the amounts of energy and magnetic flux that are transferred to the initial supervortex. In the context of the experiment, this means the specific conditions in the heating and cooling cycle, especially the heating and cooling times. A more detailed discussion of this point can be found in [13].

9.7.7 Validity and Limits of the Interpretation

Interpreting the experimental observations as stated in this discussion calls for a critical comparison with other possible explanations. As it concerns the origin of the signal, one could think of the following alternative explanations:

- Normal conducting electrons. This is unlikely because at the distance from the normal conducting spot where the large ring is observed there should be no unpaired electrons outside the vortex cores since this zone cannot be significantly heated due to its distance to the source of heat, so that these zones of the sample must be in the mixed state.

- Excited Quasiparticle States. This is unlikely for basically the same reason as stated in the context of the the possible occurrence of normal conducting electrons. The only possible source of energy for the creation of such excited states would be thermal excitation which happens too far away from the position of the observed ring structure. However, the possibility of creating such quasiparticles in the heated spot which then propagate through the sample cannot be excluded. However, since they cannot be pinned, they should not be able to create a ring structure with an open centre as the one observed. A potential distribution similar to a two-dimensional Gaussian distribution centered at the excitation spot could be expected from such a transport, if they were due to a current of quasiparticles, the same velocity argument as stated above for vortices applies: the resulting velocity would be too slow to be reasonable. It is however possible that excited quasiparticle states play a role in the creation of the inner sharp peak and its inner structure.

- Thermoelectricity due to a ring-like temperature distribution. This is also unlikely because thermal diffusion again should produce a bulb structure.
Considering these circumstances, assigning the observed signal to the vortices persists as an interpretation that appears to be likely and reasonable. Under this assumption, the observed large ring structure can be explained within the context of the presented numerical model calculations by Shapiro et al.

The model presented is however not able to explain the observed inner structure of the inner sharp peak. Further discussions and hypotheses on this question are made in [35] and [13].

9.8 Summary, Conclusions and Outlook

Using a spatially resolving detection technique, ring-shaped potential distributions have been observed in the superconducting mixed state of Nb under the conditions of periodic heating and cooling in a limited, spot-shaped zone while constantly cooling the rest of the sample by immersion in liquid $^4$He at 4.2K.

The ring structures can be explained consistently within a model based on time-dependent Ginzburg-Landau theory and thermal diffusion. Numerical model calculations performed by Shapiro et al. show the relaxation from an extended normal conducting state to a system of separate, single vortices. Under specific initial conditions, this relaxation implies the occurrence of explosive vortex nucleation at the edge of the normal conducting spot. These conditions are fulfilled in the experiment.

The initial conditions represent a situation of strong disequilibrium. The final equilibrium state is the Abrikosov vortex lattice, but the experimental observation indicates that this state is not reached in the experiment, but that the outgoing vortices are pinned and form the observed ring structures. Thus, a persistent metastable state of a type-II-superconductor has been prepared that is different from the usual Abrikosov vortex lattice. The duration of its existence is in principle not limited in time.

Since the model used to an interpretation of the experimental results is based on quite general assumptions, it can be expected that analogous phenomena can appear for other types of phase transition. In principle, any phase transition that can be described by Ginzburg-Landau theory can be expected to show a similar type of phenomenon, but their experimental observation may prove to be difficult if not a mechanism analogous to pinning exists for these phase transitions. In such a case, the experiment would have to be sensitive to the extremely short timescales of the explosive nucleation process.

A sharp peak in the potential distribution that was experimentally observed cannot be explained within the context of the vortex nucleation model. Although it can be expected that there will be some manifestation of the local heating, the experiment revealed a magnetic-field dependent inner structure of this small ring structure that cannot be explained by simple heat diffusion assumptions.
Part IV

Summary, Overall Conclusions and General Outlook / Zusammenfassung, Allgemeine Schlußfolgerungen und Ausblick
Summary, General Conclusions and Outlook

This work presents several experimental studies on superconducting systems, with an emphasis on layered organic superconductors. Three chapters out of five describing experimental results in the present work are dedicated to organic materials. However, this work does not limit itself to organic systems only. In the two subsequent chapters, a superconducting heavy fermion system is examined and in the last one, some quite general vortex dynamics phenomena have been demonstrated for the case of superconducting niobium.

Although the aspects of superconductivity treated here are of quite different nature, it is common to all experimental studies presented that they surpass the field of conventional superconductivity, that is superconductivity that can be explained within the framework of the Bardeen-Cooper-Schrieffer and equilibrium Ginzburg-Landau theories.

In the case of the organic materials, the nature of superconductivity is still not finally cleared. This work tries to contribute the efforts to understand the electronic structural properties of these systems by performing magneto-quantum oscillation experiments on the following systems:

- For $\beta$-(ET)$_2$IBr$_2$ it was shown that the beating nodes in the de Haas- van Alphen and the Shubnikov-de Haas oscillations do not appear at the same field values as it is expected from the Lifshitz-Kosevich and Adams-Holstein theories. A newly developed theory by Grigoriev has been shown to predict qualitatively the observed behaviour of the Shubnikov-de Haas node positions as it concerns their dependence on the magnetic field and the tilting angle, but cannot provide explanations for some details found experimentally. The theory limits the shift between a Shubnikov-de Haas and the corresponding de Haas- van Alphen node to a maximum of $\pi/2$ with respect to one period of the beating oscillation. However, in the experiment, shifts larger than $\pi$ could be observed. If this is due to the semiclassical approximation employed to develop the theory or if other, yet unidentified effects contribute also to the phase shift, is not yet clear. The basic assumption of the theory is to consider an additional oscillatory contribution to the resistivity that by superposition with the Shubnikov-de Haas oscillations causes the observed phase shift. This additional oscillatory contribution is supposed to be due to an oscillating electron velocity that is the consequence of the two dimensional electron dispersion. It does affect the transport properties only since it is a genuine disequilibrium phenomenon. The purely thermodynamic de Haas-van Alphen effect is not affected. In spite of some differences between theory and experiment, the qualitative accord of both the field and angular dependencies of the node shift seem to indicate that the described mechanism plays an important role. It is worth noting that in this system deviations from the Lifshitz-Kosevich theory are significant although its two dimensionality is relatively weak as it can be seen from the comparatively high beat frequency and the low harmonic content of the observed quantum oscillations.

- In $\kappa$-(ET)$_2$Cu(NCS)$_2$, deviations in the angular dependence of the apparent effective electron mass from the Lifshitz-Kosevich expectation have been shown experimentally. In a subsequent comparison of these experimental results to recent theoretical results by Champel, it was shown that modifications of the said kind could indeed occur by considering the chemical potential oscillations, as Champel did in
his calculations. They are not considered in the Lifshitz-Kosevich theory since the latter is valid for three dimensional electron systems in which chemical potential oscillations do not occur. However, the theoretical development, which is aimed at providing a general expression for the thermodynamic properties of an electronic system of arbitrary kind which would then include the Lifshitz-Kosevich results as its three-dimensional limits, is not yet at a point that would allow for a quantitative comparison with the experimental observations. Nevertheless, it can be concluded that in the shown example, the Lifshitz-Kosevich theory fails to an extend that the conventional analysis based on this theory does not make sense anymore. Moreover, the chemical potential oscillations appear to be a likely cause for this.

- The system $\alpha_T$-(ET)$_2$I$_3$ attracts interest because of its relatively high temperature for the onset of superconductivity. Moreover, the system is obtained by subjecting an essentially semiconducting system to a tempering process. Thus, structural data, on the crystalline as well as on the electronic structure, are of high interest for an understanding of the cause of the high critical temperature, moreover, they might be useful to establish connections between the structural data of a superconducting system and its superconductivity properties. In torque magnetisation experiments, indications of some residual quantum oscillation could be found, however, the system seems to consist of crystallites, whose individual magnetisation superimpose which introduces a stochastic element. This latter circumstance largely prevents a systematic analysis because it affects greatly the stability of the samples, thus leads to a lack of reproducability of the results and makes it virtually impossible to associate the observed magnetisation features with any crystalline orientation. Additional electron microscopy studies could help to establish the idea of stacked crystallites in the system, attempts for an electron focusing experiment could not yield additional information.

The significance of these experimental studies is of a manifold nature: they give information about the examined systems themselves, but more than that, they help to extend established experimental techniques to the field of unconventional superconductivity, which in turn is a necessary step on the way to a fundamental understanding of this phenomenon. The results also back up theoretical work on the subject and help to verify theoretical models. Finally, it is hoped to arrive at a concise theoretical description and experimental base of knowledge which would not be of purely scientific interest, but would also make technical applications of superconductors possible which are not feasible now.

The heavy fermion system CePd$_2$Si$_2$ also exhibits unconventional superconductivity, but this time of a three dimensional electron system and under hydrostatic pressure. This makes it possible to use straightforwardly the established analysis procedures derived from the Lifshitz-Kosevich theory. In this context, it was possible for the first time to carry out a systematic experimental study of the occurring magneto-quantum oscillations of that system, allowing for a comparison with a theoretical bandstructure model by Harima. It was found that qualitatively, the model shows the same features for the angular dependence of the quantum oscillation frequencies, but it does not correctly predict the absolute values of the frequencies. The model, however, does not take into account the metamagnetic transition that can be observed around 9...10 T in the orientation that was used in the experiment, that is rotating the sample in a plane from $\vec{H} \parallel [100]$ to $\vec{H} \parallel [110]$. Moreover,
by analysis of the effective electron mass from the de Haas- van Alphen oscillations, it has been possible to show directly the magnetic field dependence of the effective electron mass. Indications of a phase transition that occurs at about 21T for temperatures < 500 mK have also been found. This finding was totally unexpected and clearing the nature of this transition must be the object of future work.

Finally, the results on disequilibrium vortex dynamics in superconducting niobium show the possibility of metastable structures other than the Abrikosov-Vortex lattice when the system is driven to strong disequilibrium and then left to relax. This result is of a very general kind, since its theoretical description does only require classical heat conduction together with time-dependent Ginzburg-Landau theory. The latter is valid for a larger number of phase transitions than just for superconductivity. The phenomenon should also appear in systems such as superliquid helium or might even play a role for modeling the early universe. From an experimental point of view, it might be necessary to consider this effect in an accurate description of resistivity measurements on type-II-superconductors when they are still in the vortex state since the motion of the vortices is causes an energy loss and thus contributes to the resistivity. In this way, this very general experimental finding might also be considered in a refinement of the understanding of some standard experimental procedures when applying them to type-II-superconductors, an aspect that has also been discussed in other parts of this work.

Finally, it can be said that this is a contributing work: it does not give the final answer to a specific problem, but it tries to make contributions to ongoing research on a wide field that would much too large to be covered completely by a work of this kind. Instead, various aspects that seemed to be suited for being studied with the special experimental facilities at the Grenoble High Magnetic Field Laboratory have been picked out. Some contributions could be made and some unexpected findings might inspire future work.
Zusammenfassung, Allgemeine Schlußfolgerungen und Ausblick


Obwohl die Gesichtspunkte der Supraleitung so wie hier dargestellt von recht unterschiedlicher Natur sind, ist allen vorgestellten experimentellen Studien gemein, daß sie über das Gebiet der konventionellen, durch die Bardeen-Cooper-Schrieffer und Gleichgewichts-Ginzburg-Landau Theorien beschriebenen, Supraleitung hinausgehen.

Im Falle der organischen Materialien ist die Natur der Supraleitung immer noch nicht endgültig geklärt. Diese Arbeit versucht, dazu beizutragen, die elektronischen Struktureigenschaften dieser Systeme zu verstehen indem Magneto-Quantenoszillationsexperimente an den folgenden Systemen durchgeführt wurden:

- Für \( \beta-(ET)_{2}IBr_{2} \) wurde gezeigt, daß die Schwebungsknoten der de Haas- van Alphen-Oszillationen nicht bei den gleichen Feldern auftreten wie die der Shubnikov- de Haas-Oszillationen, so wie es aufgrund der Lifshitz-Kosevich und Adams-Holstein Theorien erwartet werden kann. Es wurde gezeigt, daß eine neuentwickelte Theorie von Grigoriev das Verhalten der Shubnikov-de Haas Knoten als Funktion von Magnetfeld und Orientierung qualitativ korrekt beschreibt, jedoch nicht in der Lage ist, einige experimentell gefundene Details zu erklären. Die Theorie begrenzt die Phasenverschiebung eines Shubnikov-de Haas-Knotens relativ zu dem entsprechenden de Haas-van Alphen Knoten auf maximal \( \pi \), bezogen auf eine Periode der Schwebungsoszillation. Dennoch konnten im Experiment Verschiebungen von mehr als \( \pi \) beobachtet werden. Ob dies an der semiklassischen Näherung bei Entwicklung der Theorie liegt oder ob andere, noch nicht indentifizierte Effekte ebenfalls zu der Phasenverschiebung beitragen, ist noch nicht klar. Die grundlegende Annahme der Theorie ist die Berücksichtigung eines zusätzlichen oszillatorischen Beitrages zum Widerstand der durch Überlagerung mit den Shubnikov-de Haas Oszillationen zu der beobachteten Phasenverschiebung führt. Es wird angenommen, daß dieser zusätzliche oszillatorische Beitrag aufgrund einer oszillierenden Elektronengeschwindigkeit entsteht, die ihrerseits die Folge der zweidimensionalen Dispersionsrelation ist. Dies betrifft die nur die Transporteigenschaften, da es ein Nichtgleichgewichtsphänomen im eigentlichen Sinne ist. Der rein thermodynamische de Haas-van Alphen Effekt wird nicht beeinflußt. Trotz einiger Unterschiede zwischen Theorie und Experiment scheint die qualitative Übereinstimmung von Theorie und Experiment sowohl bezüglich der Feld- wie auch der Winkelabhängigkeit anzuzeigen, daß der beschriebene Mechanismus eine wichtige Rolle spielt. Es erscheint außerdem erwähnenswert, daß in diesem System wesentliche Abweichungen von der Lifshitz-Kosevich-Theorie beobachtet werden können, obwohl sein zweidimensionaler Charakter eher schwach ausgeprägt ist, wie man an der relativ hohen Schwebungsfrequenz wie auch am ge-
ringen Anteil von Harmonischen in den beobachteten Quantenoszillationen erkennen kann.


Die Bedeutung dieser experimentellen Studien ist von vielfältiger Natur: sie ergeben Informationen über die untersuchten Systeme selbst, aber darüber hinaus helfen sie, etablierte experimentelle Techniken in den Bereich der unkonventionellen Supraleitung hinein anwendbar zu machen, was wiederum ein notwendiger Schritt auf dem Weg zu einem grundlegenden Verständnis dieser Phänomene ist. Die Ergebnisse unterstützen außerdem theoretische Arbeiten in diesem Gebiet und helfen, theoretische Modellvorstellungen zu überprüfen. Schließlich hofft man, eine umfassende theoretische Beschreibung und experimentelle Wissensbasis zu erlangen, die nicht nur von rein wissenschaftlichem Interesse
wäre, sondern auch technische Anwendungen von Supraleitern ermöglichen würde, die jetzt noch undurchführbar sind.

Das Schwerfermionensystem CePd$_2$Si$_2$ zeigt ebenfalls unkonventionelle Supraleitung, dieses Mal jedoch in einem dreidimensionalen System. Dies ermöglicht die unmittelbare Benutzung etablierter Analysemethoden, die aus der Lifshitz-Kosevich-Theorie hergeleitet werden. In diesem Zusammenhang war es erstmalig möglich, eine systematische experimentelle Studie über die Winkelabhängigkeit der auftretenden Quantenoszillationsfrequenzen dieses Systems durchzuführen, was einen Vergleich mit einem theoretischen Bandstrukturmodell von Harima ermöglichte. Hierbei wurde qualitative Übereinstimmung für die Winkelabhängigkeit gefunden, die absoluten Frequenzwerte werden jedoch nicht korrekt vorhergesagt. Darüberhinaus hat die Analyse der effektiven Elektronenmasse aus den de Haas-van Alphen-Daten es ermöglicht, die Magnetfeldabhängigkeit der effektiven Elektronenmasse unmittelbar zu zeigen. Dies ist das erste Mal, daß dies für das besagte System gezeigt werden konnte. Anzeichen eines Phasenüberganges, der für Temperaturen $\lesssim$ 500 mK bei etwa 21 T auftritt, wurden ebenfalls gefunden. Diese Entdeckung war völlig unerwartet und die Aufklärung der Natur dieses Überganges muß späterer Arbeit vorbehalten bleiben.


Abschließend kann gesagt werden, daß diese Arbeit beiträgt: sie gibt keine abschließende Antwort auf die bestimmte Frage, sie versucht vielmehr Beiträge zu einem breiten, forschenden Forschungsgebiet zu liefern, daß bei weitem zu groß ist, um von einer Arbeit wie der vorliegenden umfassend abgedeckt zu werden. Stattdessen wurden verschiedene Gesichtspunkte, die für eine Untersuchung mit den speziellen Möglichkeiten des Grenobler Hochfeldmagnetlabors geeignet schienen, herausgegriffen. Einige Beiträge konnten gemacht werden und einige unerwartete Ergebnisse mögen zukünftige Arbeit anregen.
Part V

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